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Preparation of organometallic cobalt(III) complexes containing bidentate chiral amine ligands as potential transfer hydrogenation catalysts

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Preparation of Organometallic Cobalt(III) Complexes Containing Bidentate Chiral Amine Ligands as Potential Transfer Hydrogenation Catalysts

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Abstract

Mixed coordination sphere cobalt(III) complexes containing a chiral bidentate amine ligand and an organic carbocyclic ligand have been prepared and characterized. The integration of this mixed ligand environment involving an organometallic and Werner-type ligand along with the earth abundant metal in a high oxidation state has the potential for interesting reactivity. Complexes of the type [Co(Cp^R)(X-DPEN)(I)](I), where Cp^R = cyclopentadienyl (Cp, R = H) or pentamethylcyclopentadienyl (Cp*, R = Me) and X = meso-1,2-, 1R,2R-, and 1S,2S-, have been prepared by ligand substitution from [Co(Cp^R)$(I)_2$(CO)] with 1,2-diphenyletheylenediamine (DPEN). The outer sphere iodide is readily exchangeable with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F$) or cesium acetate (CsOAc), and both iodides can be exchanged with silver(I) acetate (AgOAc). The latter reactions with AgOAc results in either [Co(Cp^R)(X-DPEN)(OH_2)]$(OAc)_2$ or [Co(Cp^R)(X-DPEN)(OAc)](OAc) depending on the solvent profile, and partial iodide removal to produce [Co(Cp*)(1S,2S-DPEN)(OAc)](I) in the presence of CsOAc. The complexes are isolated as diamagnetic black, dark purple, or, in the case of acetate complexes, pink solids and characterized by ^{1}H-NMR, ^{13}C-NMR and UV-vis spectroscopy as well as either elemental analysis or mass spectrometry. Four complexes, [Co(Cp)(1R,2R-DPEN)(I)](I) (**1**), [Co(Cp)(1S,2S-DPEN)(I)](BAr^F) (**2a**), [Co(Cp*)(1S,2S-DPEN)(I)](I) (**4**), and [Co(Cp*)(1S,2S-DPEN)(OAc)](I) (**13**) have been characterized by single-crystal X-ray diffraction. The preparation, characterization, and initial reactivity of these complexes as potential catalysts for aqueous hydrogen transfer as well as the extension to the substituted chiral amine (R,R)-*N*-(2-amino-1,2-diphenylethyl)-*p*-toluenesulfonamide (Ts-DPEN) will be discussed.

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Glossary

Bpy…… 2,2'-Bipyridine

CO……....Carbonyl (carbon monoxide)

Cp……...Cyclopentadienyl

Cp*……..Pentamethylcyclopentadienyl

Cp^R……Cp or Cp*

DPEN……..……1,2-diphenylethylenediamine

I……Iodide

OAc……Acetate

OH_2……...Aqua

Ts……Toluenesulfonyl

Chapter 1: History and Use of Cobalt and DPEN Ligand in Catalysis

1. Use of Transition Metals in Asymmetric Transfer Hydrogenation

The discovery of homogeneous transition metal catalysis made an impact in industrial chemical transfomations such as hydrogenation, hydroformylation, and polymerization reactions.[1] This has led to many new chemical processes that have technological, industrial, and medical significance. A key discovery among these transition metal catalysts was the synthesis of the so called Noyori Catalysts. In 1996, Noyori and Ikariya synthesized

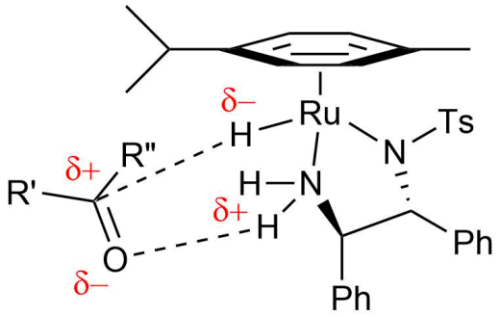
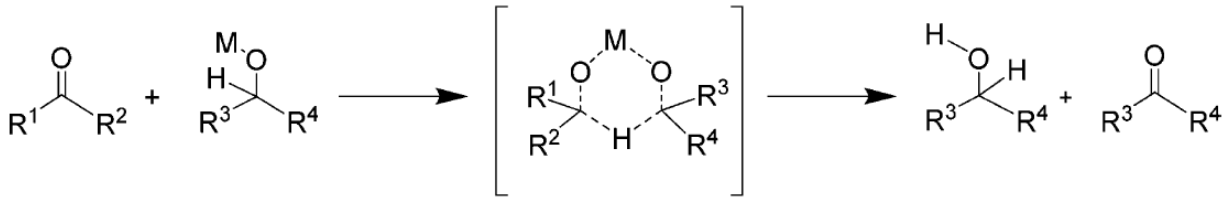


Figure 1. Noyori Catalyst

[RuCl(η^6-arene)(*N*-arylsulfonyl-DPEN)]; DPEN = 1,2-diphenylethylene-1,2-diamine (*Figure 1*), which won the Nobel Prize 2001.[2] These complexes were reported to catalyze aromatic ketones and imines with great stereoselectivity and activity using either 2-PrOH or formic acid as a hydrogen source.[2,3,4]

These metal catalysts drive the kinetics and enantioselectivity of the reaction products. In catalytic transfer hydrogenation, double bonds are reduced to single bonds with the addition of H_2 from non-gaseous H_2 sources. Transfer hydrogenation dates back to 1903 where Knoevenagel successfully used palladium to promote the disproportionation of dimethyl 1,4-dihydroterephthalate to dimethyl terephthalate and *cis*-hexahydroterephthalate.[5,6] Types of transfer hydrogenation techniques include Meerwein−Ponndorf−Verley (MPV) reductions (*Scheme 1*), late transition metal-catalyzed reactions, organocatalytic, enzyme-catalyzed,



Scheme 1. Hydrogen Transfer in the MPV Reduction via a Cyclic Transition State.[35]

thermal, and base-catalyzed, processes.[6] My research will focus on late transition metal catalyzed reactions.

A significant milestone in the study of transfer hydrogenation was the discovery of late transition metal catalysts which include second- and third-row transition metal groups.[6] For example, in the 1980s, Ru based catalysts were beginning to be synthesized and were successfully facilitating transfer hydrogenation reactions.[7,8] With the emergence of these novel

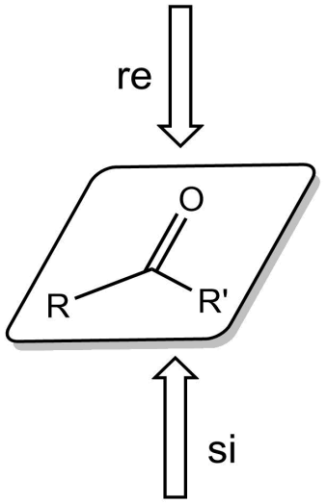
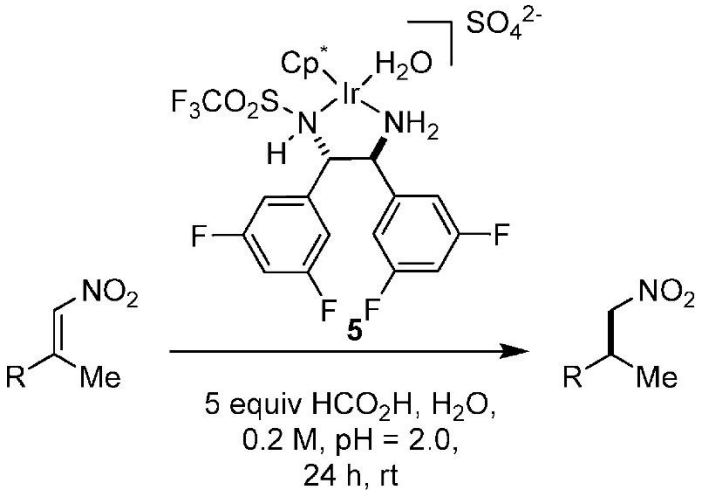


Figure 2. Ketone prochirality

catalysts, further discoveries led to the development of asymmetric transfer hydrogenation. This discovery is significant in that asymmetric hydrogenation of prochiral ketones (*Figure 2* is the most practical and simplest method to access enantiomerically enriched secondary alcohols, and this is a critical step in many pharmaceutical and other chemical processes.[9,10] It is practical in

the sense that hydrogenation requires working with flammable H_2 gas, while transfer hydrogenation requires a hydrogen source such as an alcohol. The widely used catalysts for transfer hydrogenation involve Ir, Rh, and Ru complexes in a variety of forms which include metal-*N*-heterocyclic carbenes, half sandwich, and multidentate metal complexes (*Figure 3*).[11] In addition to Ru, synthesis of Ir and Rh containing Cp* (pentamethylcyclopentadienyl) and chiral diamine ligands have been shown to catalyze transfer hydrogenation of ketones and *β, β*-disubstituted nitroalkenes (*Scheme 2*).[12,13]



Scheme 2. Asymmetric transfer hydrogenation of β,β-disubstituted nitroalkenes.[13]

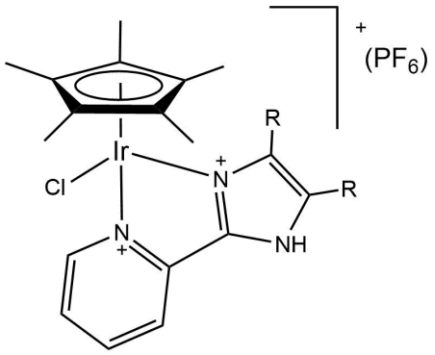


*Figure 3. An example of a transfer hydrogenation catalyst, [Cp*Ir{2-(2'-pyridyl) benzimidazole}Cl]PF_6*

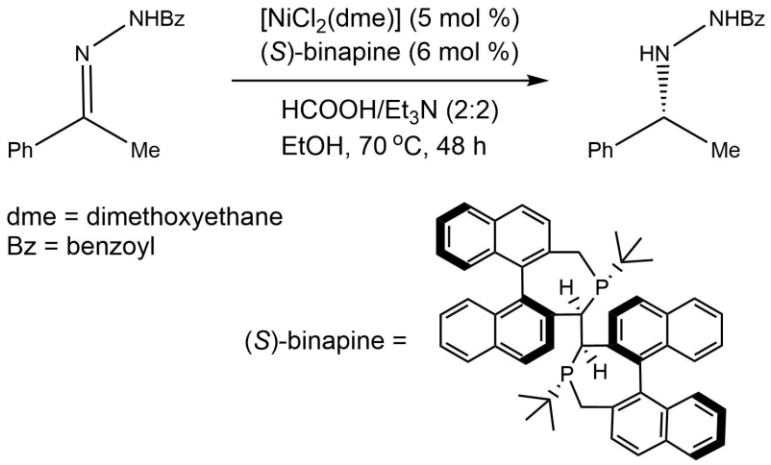
2. 1st Row Transition Metals for Catalysis

Metal	Cost per gram
Ru	$8.55
Rh	$103.20
Ir	$46.94
Co	$0.03

Table 1. Metal Prices. http://www.infomine.com/investment/precious-metals/ (as of 3/20/19)

Along with the development of Ir, Rh, and Ru based catalysts, other late transition metals have been explored and utilized for transfer hydrogenation catalysis, which includes: Au, Co, Ni, Os, Pd, Pt, and Re.[14-20] Due to variety of active metals for transfer hydrogenation, there has been a growing interest in exploring reactivities of 1st row transition metals. As mentioned before, the reduction of carbonyls, such as aldehydes, ketones, esters, carboxylic acids, and acid anhydrides, are key processes in organic chemistry. However, well-designed catalysts are mainly synthesized from precious metals such as Ir, Rh, and Ru. Because precious metals are rare, and the demand for catalysts is growing, exploring reactivities of Earth abundant metals is sensible for economic reasons as well as to reduce environmental toxicity (*Table 1*).[8,21] However, because these transition metals have access to multiple 1-electron oxidation states and weak metal to carbon bonding, it is challenging to design catalytic systems with these metals.[22]

Despite the design challenges of 1st row metal systems, several complexes have been synthesized and show catalytic activity. For example, Fe catalyzed transfer hydrogenation has been studied profusely in the last decade with great progress.[23] In 2011, the first Fe mediated transfer hydrogenation of imines was reported using the Fe precursor $[Et_3NH][HFe_3(CO)_{11}]$ in the presences of a *N*,*N*′-bis[*o*-(bis(4-trifluoromethylphenyl)phosphino)benzylidene]-(1*S*,2*S*)-diaminocyclohexane (PNNP) ligand.[24] Another example is the Fe catalyzed homogeneous hydrogenation of alkenes using $(PNHP^{iPr})Fe(H)_2(CO)$ ($PNHP^{iPr}$ = $NH(CH_2CH_2P\textit{i}Pr_2)_2$), which was done under mild conditions.[25] Ni based catalysts have also been synthesized and shown



Scheme 3. Nickel-Catalyzed Asymmetric Transfer Hydrogenation of Hydrazones

activity in the reduction of unsaturated compounds via transfer hydrogenation (*Scheme 3*).[26]

3. Cobalt in Catalysis

For the project described in subsequent chapters, we are interested in the design of Earth abundant metals for catalysis to possibly improve the current method of hydrogenation. Current literature reveals that there are cobalt based systems that facilitate hydrogenation reactions. One design includes the preparation of C_1-symmetric bis-(imino) pyridines in which one imine is secured by a large 2,6-diisopropylaryl ring and the other is arranged from a single enantiomer of a chiral alkyl amine (*Figure 4*).[27] The complex is activated in the presence of H_2 to release methane and make a Co(I) hydride.[28] The oxidation state of the metal remains the same during the catalytic reaction.

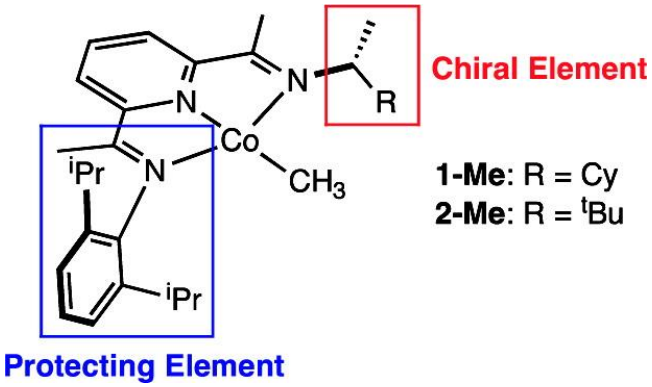


Figure 4. enantiopure, C_1-symmetric bis(imino)pyridine Co(I) methyl complexes for asymmetric olefin hydrogenation.[27]

Moreover, carbon dioxide can be thermally reduced to methanol using a homogeneous cobalt-based catalyst. Jacob Schneidewind and coworkers have developed the first homogenous non-noble metal catalyst for the hydrogenation of CO_2 to methanol. Their catalyst design is developed from $[Co(acac)_3]$, where acac = acetylacetone, Triphos (bis(diphenylphosphinoethyl)phenylphosphine), and $HNTf_2$ (triflimide).[29] The use of this complex allows the hydrogenation reaction to run at 100 $^{\circ}$C without decreasing any catalytic activity. All of the chemical systems mentioned indicate that cobalt has unique properties that drives its catalytic potential. The oxidation states of the metal do not change since the ligands are

redox active and facilitate the catalytic reactions. Our proposed system will be different as we will be working with Co(III) and and will utilize the DPEN ligand for an H^+ and the Co-H as H^- as reported for the Noyori catalyst.[2]

4. Use of Cobalt with Achiral and Chiral Amine Ligands

Co(III)-DPEN (DPEN = 1,2-diphenylethylenediamine) compounds have been synthesized and been utilized for catalysis. These compounds have been reported to facilitate asymmetric C-C bond forming reactions.[30] These compounds are a derivative of the Werner compounds, which were the first inorganic compounds that were resolved enantiomerically about a century ago.[31] The $[Co((S,S)\text{-}DPEN)_3]^{3+}$ 3X– ((S,S)-3^{3+} 3X–; X = Cl, ClO_4) compounds were able to catalyze Michael addition of malonate esters to nitroalkenes in high enantioselectivity without the need of an inert atmosphere environment.

Co(III) mixed sandwich complexes of the type $[Co(Cp^R)([9]aneX_3)](PF_6)_2$, where $[9]aneX_3$ = thioether ($[9]aneS_3$) or azaether ($[9]aneN_3$), have been prepared from $[Co(Cp^R)(CO)(I)_2]$ which includes the organometallic cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) ligands.[32] These complexes show the lability of CO and iodide ligands are labile and therefore can serve as synthetic starting point for a mixed coordination sphere. Our proposed complex includes an organometallic ligand, Cp and/or Cp* and the Werner DPEN ligand. The addition of a hydride to the complex $[Co(Cp^R)(X,X\text{-}DPEN)(I)](I)$ will also explored as it plays a key role in transfer hydrogenation. However, isolation and characterization of Co(III)-H complexes are rare, which makes these complexes interesting from a structural viewpoint.[33,34] These examples give rationale to further explore Co(III) as a potential catalyst for transfer hydrogenation reactions and the proposed complex will be discussed in the next chapter.

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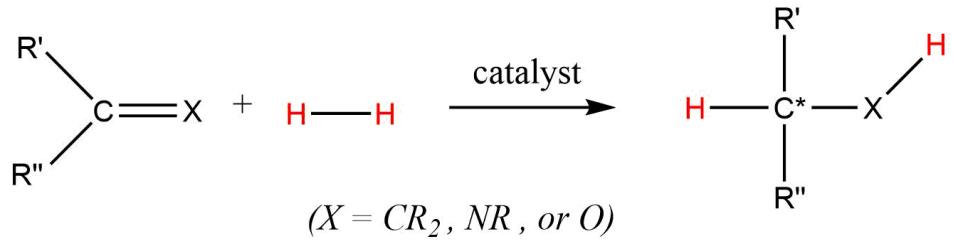
Chapter 2: Synthesis and reactivity of Co(III) complexes with bidentate amine ligands for catalytic asymmetric transfer hydrogenation

1. Introduction

The purpose of this research is to develop a cobalt(III) catalyst to facilitate homogenous asymmetric hydrogenation (*Scheme 1*). Currently, the majority of the catalysts being used are precious metals such as ruthenium, rhodium, and iridium.[1] These reactions are responsible for synthesizing biochemical compounds that can be useful for making pharmaceutical drugs (*Scheme 2)*.[2] For example, Noyori et. al. developed a ruthenium system featuring Ts-DPEN and *para*-cymene ligands, and others have used this as a starting point to make changes to the chiral



Scheme 1. Selective preparation of chiral alkanes, alcohols or amines from prochiral ketones and imines

ligand that is able to catalyze asymmetric hydrogenation reactions (*Figure 1*).[3] My goal is to replace expensive metals with first-row transition metals by attempting to extend this chemistry to Earth-abundant Co(III) homogeneous complexes. This is proposed to be accomplished by taken advantage of the affinity of Co(III) for sp^3-hybridized-amine ligands, which are present in the Noyori catalyst, and the subsequent inertness of the Co-N bond.[4,5]

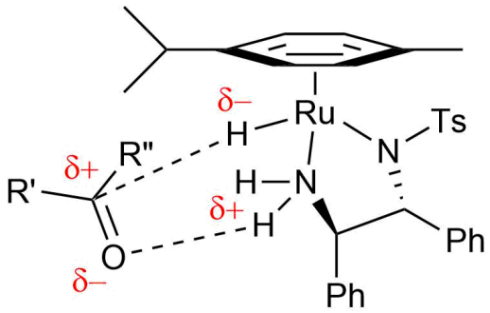
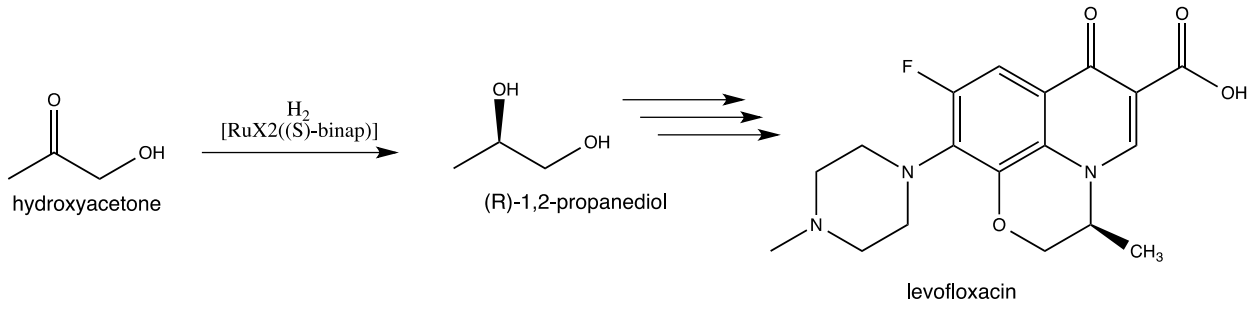


Figure 1. Noyori Catalyst

It would be beneficial to switch to first–row transition metals as they are more abundant and thus more cost effective. Indeed, finding ways to replace precious metals with Earth abundant metal-based catalysts is a growing field among synthetic chemists.[1] The synthesis of enantiopure compounds using abundant Earth metals is challenging due to the redox flexibility of the metal (i.e., many1-electron oxidation states are typically available). However, literature suggests that cobalt complexes containing chiral ligands have been synthesized and has been used for asymmetric alkene hydrogenation reactions.[1,6]



Scheme 2. Synthesis of Levofloxacin

A mixed coordination sphere cobalt complex was successfully synthesized by our group and has been fully characterized excluding ^{13}C NMR (*Figure 2).* The complex features the addition of a stabilizing anionic cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) to occupy three coordination sites of the octahedral complex, which will direct reactivity, similar to the

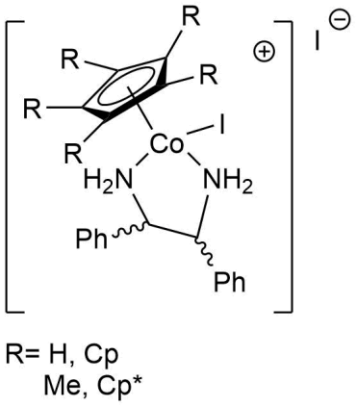


Figure 2. [Co(Cp^R)(X,X-DPEN)(I)](I)

aromatic *p*-cymene ligand on the Noyori catalyst. Also, the complex contains a 1,2-diphenylethane-1,2-diamine (DPEN) chiral ligand which will provide an asymmetric environment and a proton source. Lastly, the complex contains an iodide in both the inner sphere bound to the Co(III) and outer sphere with the former likely to be labile and the latter to potentially provide unique solubility opportunities via anion exchange.

Transfer hydrogenation, as mentioned already, involves the addition of H_2 across a C-C double bond. Although H_2 in of itself is a cleaner gas than hydrocarbons, there are environmental issues during modern production of H_2 gas. Currently, 90% of H_2 production is done by steam reforming of natural gas or high temperature oil fraction.[7] H_2 production from natural gas, however, is always associated with greenhouse gas emissions.[8] For this reason, alternative sources H_2 have been of most interest among chemists and environmental researchers. The two main alternatives include H_2O splitting as well as electrocatalytic CO_2 reduction. However, these have their challenges as well due to high activation energies.[9]

A key step in the preparation of a transfer hydrogenation catalyst from [Co(CpR)(X,X-DPEN)(I)](I) will be the synthesis of a cobalt hydride (Co-H). The isolation and synthesis of substituting the inner sphere iodide with a hydride to the complex will be challenging as Co(III) hydride as isolated examples are rare.[10]

2. Experimental Section

2.1. Materials

All solvents and reagents were used as received. The ligands R,R-DPEN, S,S-DPEN, as well as both silver acetate (AgOAc) and sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate ($NaBAr^F$) were purchased from either Aldrich Chemical Company or Acros Organics and used as received. The metal reagents $[Co(Cp)(CO)(I)_2]$ and $[Co(Cp^*)(CO)(I)_2]$ were prepared as previously reported.[11,12]

2.2. Measurements

^1H and ^{13}C NMR spectra were obtained on a JEOL ECX 400 MHz spectrometer (operating frequency for ^{13}C NMR was 100 MHz) and referenced against tetramethylsilane using residual proton signals (^1H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). UV-vis spectra were obtained on a Varian Cary UV-vis spectrophotometer in dichloromethane using 1 cm quartz cuvettes. Elemental analyses were performed by Atlantic Microlab, Inc in Norcross, GA. Mass spectra were obtained via electrospray ionization on a Waters Quattro Micro quadrupole mass spectrometer operated in the positive mode with a 2.0 kV capillary and 35 V cone voltage. Samples dissolved in acetonitrile were introduced at a flow rate of 22 µL/min using the direct infusion syringe pump. Mass spectra were obtained over the range m/z 200 – 1400 with a scan speed of 1200 amu/sec.

2.3.Syntheses

*2.3.1. Preparation of [Co(Cp)(R,R-DPEN)(I)](I) (**1**).*

A 50 mL round-bottom flask was charged with $[Co(Cp)(CO)(I)_2]$ (0.1027 g, 0.2531 mmol) and toluene (20 mL). To the dark purple solution was added (1R,2R) diphenylethylenediamine (R,R-DPEN) (0.0658 g, 0.310 mmol), and the mixture was allowed to

stir at room temperature for approximately 24 h under a nitrogen atmosphere. The volatiles were reduced *in vacuo*, leaving a dark purple residue, and hexanes were used to precipitate a solid product. The dark purple solid was collected by vacuum filtration and dried *in vacuo*. The final product weighed 0.141 g, 95% yield. ^{1}H NMR (3a-1H-LD), ^{13}C NMR (3a-13C-LD). ^{1}H NMR ($CDCl_3$, δ): 5.85 (5H, s, Cp), 4.33 (1H, td, CH), 3.38 (1H, td, CH), 3.30 (1H, t, NH), 4.60 (1H, s, NH), 7.21-7.32 (8H, m, DPEN aromatic and NH). ^{13}C {^{1}H} NMR ($CDCl_3$, δ): 129.3, 129.1, 129.0, 128.9, 128.7, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 128.0 (12C, DPEN aromatic C), 83.8 (5C, Cp), 64.9 (1C, CH), 63.7 (1C, CH). Anal. Calcd for $C_{19}H_{21}N_2I_2Co$: H, 3.59; N, 4.75. Found: H, 3.84; N, 5.10. UV-Vis (CH_2Cl_2, nm ($L•M^{-1}cm^{-1}$)): 555 (1130), 279 (22800).

*2.3.2 Preparation of [Co(Cp)(S,S-DPEN)(I)](I) (**2**).*

A 50 mL round-bottom flask was charged with [Co(Cp)(CO)$(I)_2$] (0.109 g, 0.268 mmol) and dichloromethane (20 mL).To the dark purple solution was added (1S,2S)-diphenylethylenediamine (S,S-DPEN) (0.0691 g, 0.326 mmol), and the mixture was allowed to stir at room temperature for approximately 24 h under a nitrogen atmosphere. The volatiles were reduced *in vacuo*, leaving a dark purple residue, and hexanes were used to precipitate a solid product. The dark purple solid was collected by vacuum filtration and dried *in vacuo*. The final product weighed 0.135 g, 85% yield. ^{1}H NMR (7b-1H-LD) ^{13}C NMR (33b-13C-JM). ^{1}H NMR ($CDCl_3$, δ): 6.06 (5H, s, Cp), 4.71 (1H, m, CH), 3.53 (1H, m, CH), 5.25 (1H, m, NH), 7.17-7.30 (9H, m, DPEN aromatic and NH). ^{13}C {^{1}H} NMR (CD_3CN, δ): 128.4-130.0 (12C, DPEN aromatic C), 84.6 (5C, Cp), 65.7 (1C, CH), 64.6 (1C, CH). Anal. Calcd for $C_{19}H_{21}N_2I_2Co$: C, 31.74; H, 4.46. Found: C, 31.15; H, 4.51. UV-Vis (CH_2Cl_2, nm ($L•M^{-1}cm^{-1}$)): 576 (1290), 295 (24800).

2.3.3 Preparation of [Co(Cp)(R,R-DPEN)(I)](I) (**3**).*

A 50 mL round-bottom flask was charged with [Co(Cp*)(CO)$(I)_2$] (0.110 g, 0.230 mmol) and dichloromethane (20 mL). To the dark purple solution was added (1R,2R)-diphenylethylenediamine (R,R-DPEN) (0.0612 g, 0.288 mmol), and the mixture was allowed to stir at room temperature for approximately 24 h under a nitrogen atmosphere. The volatiles were reduced *in vacuo*, leaving a dark purple residue, and hexanes were used to precipitate a solid product. The dark purple solid was collected by vacuum filtration and dried *in vacuo*. The final product weighed 0.119 g, 86% yield. ^{1}H NMR (1f-1H-LD), ^{13}C NMR (1a-13C-LD). ^{1}H NMR (acetone-d_6, δ): 1.97 (15H, s, Cp*), 3.70 (1H, td, CH), 4.57 (1H, td, CH), 3.88 (1H, t, NH), 4.71 (1H, t, NH), 5.41 (1H, t, NH), 6.08 (1H, t, NH), 7.18-7.30 (12C, m, DPEN aromatic CH). ^{13}C{^{1}H} NMR (CD_3CN, δ): 11.1 (5C, Cp* aromatic CH_3), 63.7 (1C, CH), 65.0 (1C, CH), 93.6 (5C, Cp* aromatic C), 138.5, 137.6, 128.7, 128.7, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9 (12C, DPEN aromatic C). Anal. Calcd for $C_{19}H_{21}N_2I_2Co$: H, 4.73. Found: H, 5.02. UV-Vis (CH_2Cl_2, nm ($L•M^{-1}cm^{-1}$)): 565 (1170), 358 (4540), 289 (25900).

2.3.4 Preparation of [Co(Cp)(S,S-DPEN)(I)](I) (**4**).*

A 50 mL round-bottom flask was charged with [Co(Cp)(CO)$(I)_2$] (0.107 g, 0.225 mmol) and dichloromethane (20 mL). To the dark purple solution was added (1S,2S)-diphenylethylenediamine (S,S-DPEN) (0.0594 g, 0.280 mmol), and the mixture was allowed to stir at room temperature for approximately 24 h under a nitrogen atmosphere. The volatiles were reduced *in vacuo*, leaving a dark purple residue, and hexanes were used to precipitate a solid product. The dark purple solid was collected by vacuum filtration and dried *in vacuo*. The final product weighed 0.0666g, 45% yield. ^{1}H NMR (2b-1H-LD), ^{13}C (2a-13C-LD). ^{1}H NMR (CD_3CN, δ): 1.75 (15H, s, Cp*), 4.11 (1H, td, CH), 3.51 (1H, td, CH), 3.91 (1H, t, NH), 4.66

(1H, d, NH), 5.06 (1H, d, NH), 7.12-7.25 (11H, m , DPEN aromatic and NH). ^{13}C {^{1}H} NMR (CD_3CN, δ): 137.9, 137.1, 129.6, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.2, 127.7 (12C, DPEN arom. C), 93.6 (5C, Cp* arom. C), 64.6 (1C, CH), 64.2 (1C, CH), 11.1 (5C, Cp* arom. CH_3). Anal. Calcd for $C_{19}H_{21}N_2I_2Co$: C, 43.65; H, 4.73; N, 4.24. Found: C, 43.36; H, 4.91; N, 4.44. UV-Vis (CH_2Cl_2, nm ($L•M^{-1}cm^{-1}$)): 565 (1230), 357 (4150), 288 (24600).

*2.3.5. Preparation of [Co(Cp)(meso-DPEN)(I)](I) (**5**).*

A 50 mL round-bottom flask was charged with [Co(Cp)(CO)$(I)_2$] (0.103 g, 0.253 mmol) and dichloromethane (15 mL). To the dark purple solution was added meso-1,2-diphenylethylenediamine (meso-DPEN) (0.0690 g, 0.325 mmol), and the mixture was allowed to stir at room temperature for approximately 24 h under a nitrogen atmosphere. The volatiles were reduced *in vacuo*, leaving a black residue, and hexanes were used to precipitate a solid product. The black solid was collected by vacuum filtration and dried *in vacuo*. ^{1}H NMR (32a-1H-JM), ^{13}C (32b-13C-JM). ^{1}H NMR ($CDCl_3$, δ): 5.86 (5H, s, Cp), 6.22 (2H, m, CH or NH), 4.59 (2H, m, CH or NH), 4.06 (1H, m, CH or NH), 7.05-7.36 (15H, m, DPEN aromatic). ^{13}C {^{1}H} NMR (CD_3CN, δ): 135.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.9, 127.0, 127.7, 127.6, 127.5 (12C, DPEN aromatic C), 84.6 (5C, Cp), 65.7 (1C, CH), 64.6 (1C, CH). Data suggest two diastereomers in a 10:1 ratio.

2.3.6 Attempted Preparation of [Co(Cp)(meso-DPEN)(I)](I) (**6**).*

A 50 mL round-bottom flask was charged with [Co(Cp*)(CO)$(I)_2$] (0.102 g, 0.214 mmol) and dichloromethane (15 mL). To the dark purple solution was added meso-1,2-diphenylethylenediamine (meso-DPEN) (0.0545 g, 0.257 mmol), and the mixture was allowed to stir at room temperature for approximately 24 h under a nitrogen atmosphere. The volatiles were reduced *in vacuo*, leaving a purple residue, and hexanes were used to precipitate a solid product.

The purple solid was collected by vacuum filtration and dried *in vacuo* ^{13}C {^{1}H} NMR (CD_3CN, δ) 93.0 (5C, s, Cp), 92.7 (5C, s, Cp), 63.3 (1C, s, DPEN), 59.3 (1C, s, DPEN), 12.0 (5C, s, Cp* CH_3). Data suggest two diastereomers in a 1:2 ratio.

*2.3.7. Preparation of [Co(Cp)(S,S-DPEN)(I)](BAr^F) (**2a**)*

A 10 mL round-bottom flask was charged with [Co(Cp)(S,S-DPEN)(I)](I) (0.0104 g, 0.0176 mmol), dichloromethane (3mL), NaBAr^F (0.0241 g, 0.0272 mmol), and H_2O (3 mL). The dark purple mixture was vigorously stirred for 2 h at 35°C. The organic phase was separated and was evaporated. ^{1}H NMR (32a-1H-LD), ^{13}C NMR (32a-13C-LD) (0.0181 g). ^{1}H NMR (acetone-d_6, δ): 7.77 (14H, m, ortho-H BAr^F), 7.66 (7H, s, para-H BAr^F), 7.15-7.32 (12H, m, DPEN aromatic and NH), 6.78 (1H, t, NH), 5.95 (5H, s, Cp), 5.42 (1H, t, NH), 4.56 (1H, td, CH), 3.70 (1H, t, NH), 3.46 (1H, td, CH).^{13}C {^{1}H} NMR (acetone-d_6, δ): 161.8 (4C, quartet, C-B), 134.7, 129.7, 129.3, 129.1, 129.3, 128.9, 128.9, 128.7, 128.6, 127.9, 127.4 (11C, m, ortho-C BAr^F and DPEN aromatic) 124.5 (4C, quartet, CF_3), 85.0 (5C, Cp), 66.3 (1C, CH), 64.5 (1C, CH). Anal. Calcd for $C_{51}H_{33}N_2BCoF_{24}I_2$: C, 46.18; H, 4.73; N, 2.11. Found: C, 46.28; H, 2.64; N, 2.06.

2.3.8. Preparation of [Co(Cp)(R,R-DPEN)(I)](BAr^F) (**3a**)*

50 mL round-bottom flask was charged with [Co(Cp*)(R,R-DPEN)(I)](I) (0.1758 g, 0.2663 mmol), dichloromethane (15 mL), NaBAr^F (0.3539 g, 0.3993 mmol), and H_2O (15 mL). The dark purple mixture was vigorously stirred for 2 h at 35°C. The organic phase was separated and was evaporated. ^{1}H NMR (37d-1H-LD). ^{1}H NMR(acetone-d_6, δ): 7.79 (18H, m, ortho-H BAr^F), 7.67 (9H, s, para-H BAr^F), 7.12-7.48 (16H, m, DPEN aromatic), 5.95 (1H, t, NH), 5.42 (1H, s, NH), 4.77 (1H, t, NH), 4.37 (1H, td, CH), 3.97 (1H, t, NH) 3.66 (1H, td, CH), 1.94 (15H, s, Cp*). Anal. Calcd for $C_{56}H_{43}N_2BCoF_{24}I_2$: C, 47.38; H, 2.77; N, 1.97. Found: C, 48.01; H, 2.79 ; N, 1.63.

2.3.9 Preparation of [Co(Cp)(S,S-DPEN)(I)](BAr^F) (**4a**).*

50 mL round-bottom flask was charged with [Co(Cp*)(S,S-DPEN)(I)](I) (0.0706 g, 0.1069 mmol), Dichloromethane (15 mL), NaBAr^F (0.1427 g, 0.1610 mmol), and H_2O (15 mL). The dark purple mixture was vigorously stirred for 1.5 hr at 35°C. The organic phase was separated and was reduced *in vacuo.* A dark purple solid was isolated. The final product weighed 0.092 g. ^{1}H NMR (41a-1H-LD). ^{1}H NMR(acetone-d_6, δ): 7.79 (21H, m, ortho-H BAr^F), 7.67 (10H, s, para-H BAr^F), 7.12-7.48 (18H, m, DPEN aromatic), 5.95 (1H, t, NH) 5.41 (1H, t, NH), 4.77 (1H, t, NH), 4.38 (1H, td, CH), 3.96 (1H, t, NH) 3.68 (1H, td, CH), 1.94 (15H, s, Cp*). Anal. Calcd for $C_{56}H_{43}N_2BCoF_{24}I_2$: C, 47.38; H, 2.77; N, 1.97. Found: C, 48.18; H, 3.12; N, 1.67.

2.4.10. Attempted Preparation of [Co(Cp)(R,R-DPEN)(CH_3)]I*

From the glovebox, a 100 mL round-bottom flask was charged with **3** (0.0603g, 0.0913 mmol), dichloromethane (20 mL), and granulated Zn (0.0315 g, 0.481 mmol). The dark purple solution was stirred at either room temperature or reflux for ~22 h. A solid, presumably ZnI, was removed from solution through filtration. The filtrate was collected. CH_3I (0.15 mL, 5 mol equivalent) was then added to the solution. There were no observable color changes. The solution stirred for 3 h and formed a cloudy precipitate. Solution was dried under *vacuo* until a solid was isolated. The final product weighed 0.053g. ^{1}H NMR (9a-1H-LD). The NMR spectra revealed that the complex was paramagnetic, and therefore there were no significant peaks to be observed.

2.4.11. Attempted Catalytic Preparation of dimethyl 2-(2-nitro-1-phenylethyl) malonate

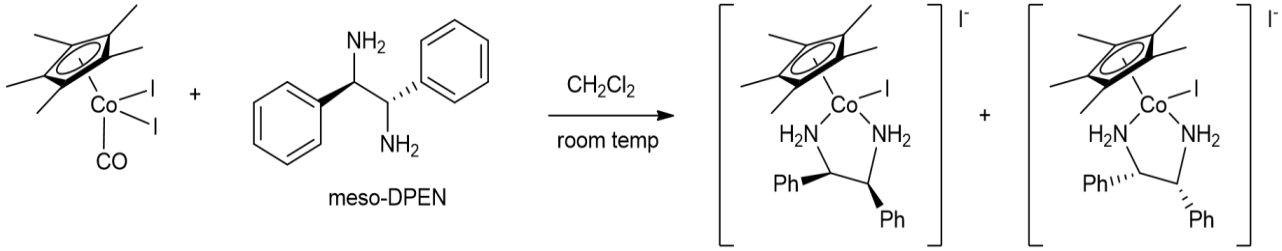
A ^{1}H NMR of dimethyl malonate (a) and *trans*-β-nitrostyrene (b) were obtained separately. Added (a) (0.004 mL, 0.0352 mmol) and (b) (0.0053g, 0.0355 mmol) into a vial and dissolved them in 0.75 mL acetone-d_6. Added **4a** (0.005g, 0.0035 mmol) into the solution. The solution was then transferred to a screw cap NMR tube. Added triethylamine (0.005 mL, 0.0356 mmol) to the solution and was left at room temperature for ~3.5 h. A slight color change occurred from dark to light purple. After 72 h, the solution color changed to red-orange. ^{1}H NMR (84a-1H-LD). There were no observable changes in the organic substrates per NMR spectra.

2.5. X-Ray Crystallography Data Collection and Processing

Appendix A contains crystal data, collection parameters, and refinement criteria for the crystal structures of **1**, **2a**, and **4**. All crystals were grown by diffusion of diethyl ether into a dichloromethane solution of the complex, or hexane layering onto a dichloromethane solution of the complex. Crystals were mounted on the tip of a Bruker SPINE-pin mount and X-ray intensity data were measured at low temperature using an Oxford Cryosystems Desktop Cooler (200(2) K) for all structures with a graphite monochromated Mo kα radiation (λ = 0.71073 Å) on a Bruker SMART X2S Benchtop diffractometer. Integration, data reduction and scaling were carried out with the programs SAINT and SADABS in the Bruker APEX2 suite of software. Each structure was solved (XS) using direct methods and refined using full matrix least squares refinement (SHELXL2017) within Olex2. A direct-methods solution was calculated that provided the non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All of the hydrogen atoms in each structure were placed in ideal positions and refined as riding atoms.

3. Results and Discussion – Part 1 Synthesis and Characterization

Synthesis of [Co(Cp^R)(X,X-DPEN)(I)](Y)



Scheme 3. Synthesis of [Co(Cp*)(meso-DPEN)(I)](I)

The classic coordination chemistry of studies by Werner with Co(III) and amine ligands showed the affinity of Co(III) for amine ligands,[4,5] and with the lability of the CO and I (with bidentate ligands) on complex [Co(Cp^R)(CO)(I)$_2$] , our starting point was meso-DPEN in order to optimize synthetic procedure due to the low cost of the ligand. Complexes of the type [Co(Cp*)(P-P)I]I had been successfully prepared where P-P is a bidentate phosphine.[13] Optimization reactions were performed for both Cp (**5**) and Cp* (**6**) starting [Co(Cp^R)(CO)(I)$_2$] complexes. The products are isolated as black or purple solids for [Co(Cp)(meso-DPEN)(I)]I (**5**) and [Co(Cp*)(meso-DPEN)(I)]I (**6**), respectively, with the Cp* shown in *Scheme 3*. As shown by NMR spectroscopy, the reaction of the meso ligand with [Co(Cp^R)(CO)(I)$_2$] results in the isolation of a mixture of two diastereomers (*Scheme 3*) where the ratio is sterically driven and the Cp complex is a 1:10 ratio of products while the Cp* complex is a 1:2 ratio as observed by ^{13}C NMR spectroscopy. Seven resonances are expected in the ^{13}C NMR for both complexes. However, fourteen resonances are observed. Furthermore, based on relative peak heights, this is representative of a 2:1 ratio of diastereomers where all ^{1}H and ^{13}C NMR resonances have been resolved for both complexes (*Figures 3* and *4*).

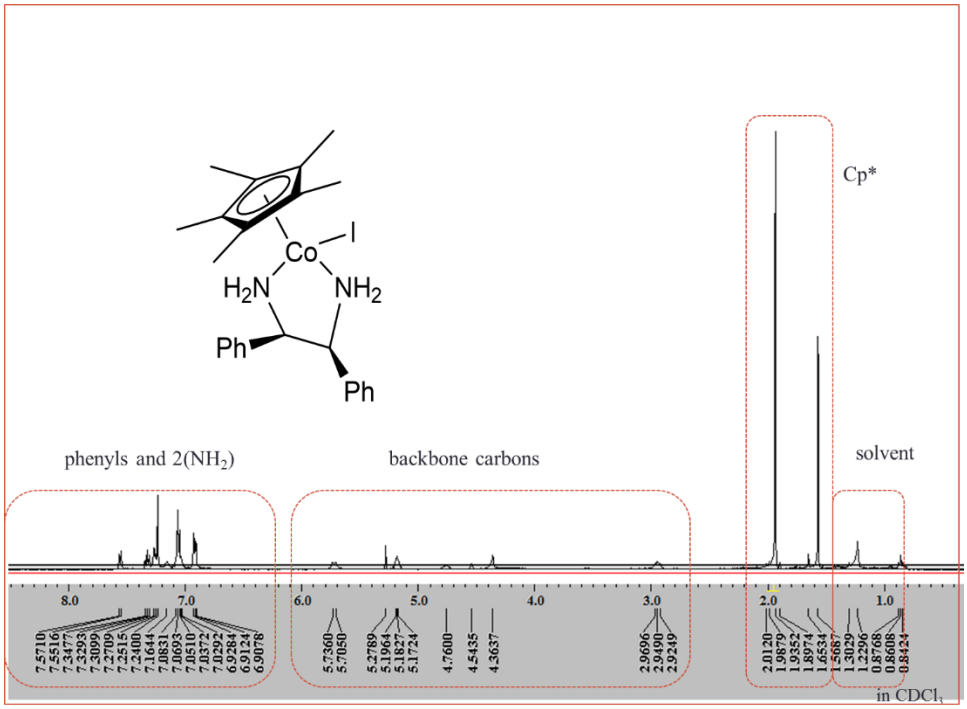


Figure 3. ^{1}H NMR of [Co(Cp)(meso-DPEN)(I)](I)*

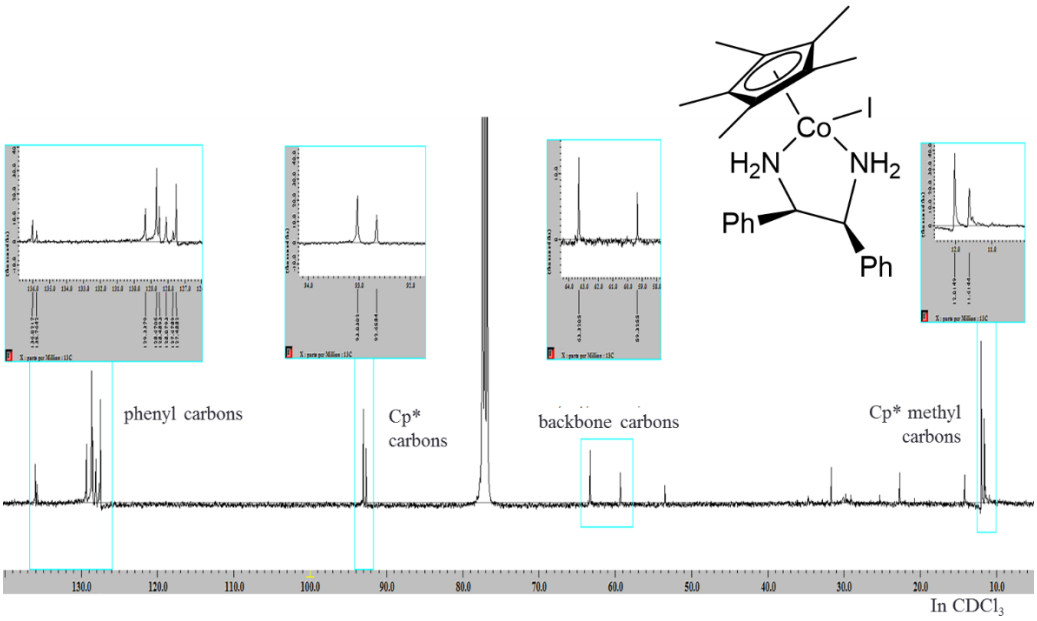
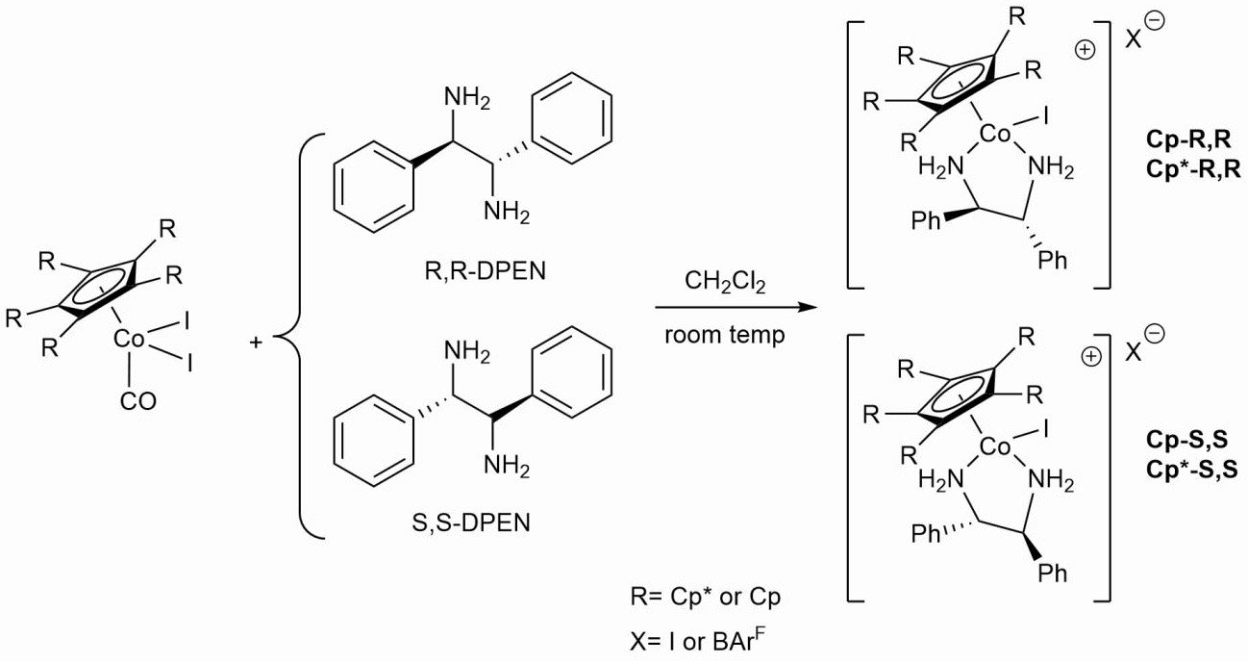


Figure 4. ^{13}C NMR of [Co(Cp)(meso-DPEN)(I)](I)*

Our focus then shifted to explore the synthesis and characterization of the complexes containing (R,R)- and (S,S)- DPEN. These complexes are also prepared via ligand substitution between the carbonyl and iodide ligands of $[Co(Cp^R)(CO)(I)_2]$ with diphenylethylenediamine (DPEN) in an inert N_2 environment (*Scheme 4*) to produce [Co(Cp)(R,R-DPEN)(I)](I) (**1**), [Co(Cp)(S,S-DPEN)(I)](I) (**2**), [Co(Cp*)(R,R-DPEN)(I)](I) (**3**), [Co(Cp*)(S,S-DPEN)(I)](I) (**4**). Complees [Co(Cp)(S,S-DPEN)(I)](BAr^F) (**2a**), [Co(Cp*)(R,R-DPEN)(I)](BAr^F) (**3a**), and [Co(Cp*)(S,S-DPEN)(I)](BAr^F) **4a** are prepared by a subsequent anion exchange (*Scheme 5*). The complexes are isolated as purple colored solids in 45%-95% yield and have been fully characterized excluding ^{13}C NMR. As shown in *Scheme 5*, the outer sphere iodide can be exchanged with $NaBAr^F$ to aid in recrystallization.



Scheme 4. Synthesis of $[Co(Cp^R)(X,X\text{-}DPEN)(I)](Y)$

Complexes [Co(Cp)(R,R-DPEN)(I)](I) **1** and [Co(Cp)(S,S-DPEN)(I)](I) **2** were confirmed by ^{1}H and ^{13}C NMR (*Figure 5*). There are negligible differences between NMR spectra when using either R,R or S,S DPEN enantiomers, but differences are observed in Cp versus Cp*. The ^{1}H NMR spectra revealed a singlet at 5.85 (**1**), 6.06 ppm (**2**), integrating for five protons, which corresponds with the Cp ligand. The two methine groups from the DPEN resonances are chemically different due to the lack of a mirror plane and resonate at 3.38 (**1**), 3.53 ppm (**2**), and 4.33 (**1**), 4.71 ppm (**2**) as triplet of doublets. The triplet rises from the CH coupling to the amine protons and the doublet from coupling to one adjacent CH proton. The ^{13}C NMR spectra revealed a singlet at 83.8 (**1**), 84.6 ppm (**2**), which corresponds with the Cp ligand. The resonances for the two methines on the DPEN appeared at 63.7 (**1**), 64.6 ppm (**2**), and 64.9 (**1**), 65.7 ppm (**2**) as singlets. There are negligible differences between the spectra when using either R,R or S,S DPEN enantiomers.

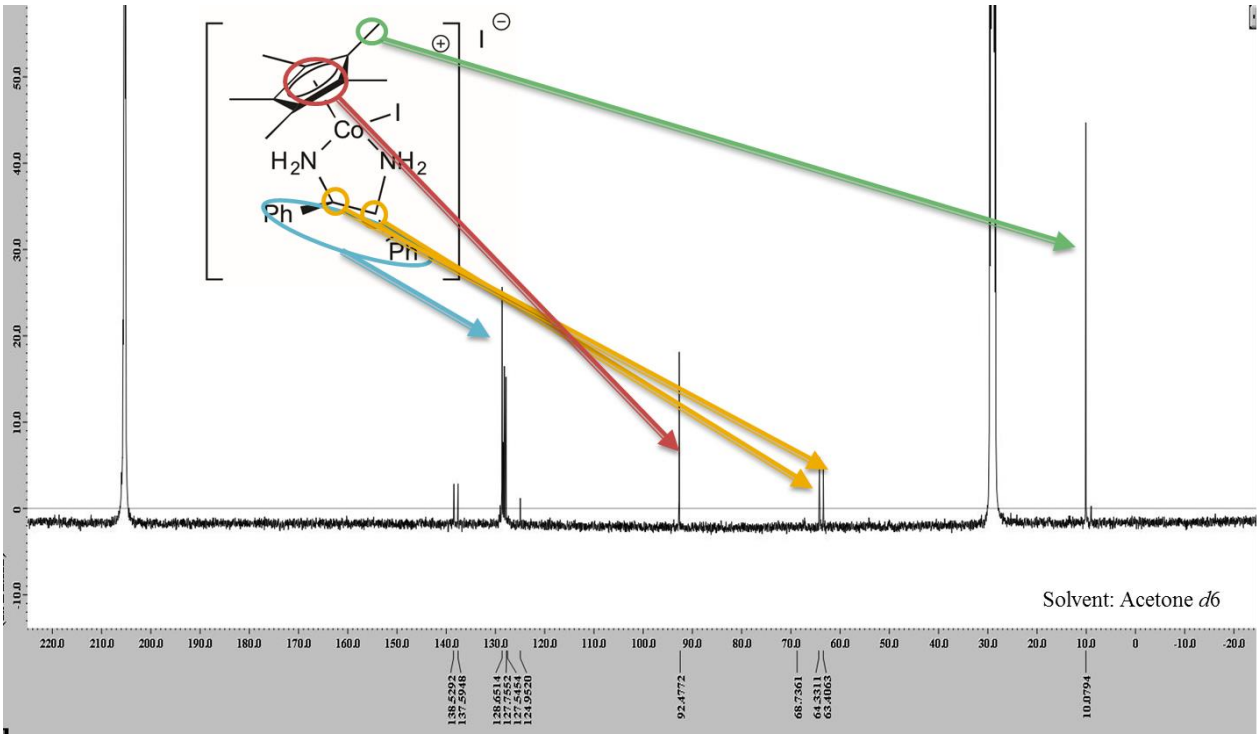


Figure 5. ^{13}C NMR of [Co(Cp)(R,R-DPEN)(I)](I)*

Complexes [Co(Cp*)(R,R-DPEN)(I)](I) **3** and [Co(Cp*)(S,S-DPEN)(I)](I) **4** were confirmed by ^{1}H and ^{13}C NMR. The ^{1}H NMR spectra revealed a singlet at 1.97 (**3**), 1.75 ppm (**4**), integrating for fifteen protons, which corresponds with the Cp* analogue. The two methine groups from the DPEN resonances were revealed at 3.70 (**3**), 3.51 ppm (**4**), and 4.57 (**3**), 4.11 ppm (**4**). The ^{13}C NMR spectra revealed a singlet at 93.6 (**3**), 93.6 ppm (**4**), which corresponds with the Cp* aromatic C analogue. The resonances for the methyl groups on the Cp* appeared at 11.1 (**3**), 11.1 ppm (**4**). The two methine carbon resonances appeared at 63.7 (**3**), 64.1 ppm (**4**), and 65.0 (**3**), 64.6 ppm (**4**). A ^{1}H-^{13}C HMQC NMR spectrum confirmed the assignments for the DPEN methine backbone in ^{1}H and ^{13}C NMR spectra for **3** (*Figure 6*).

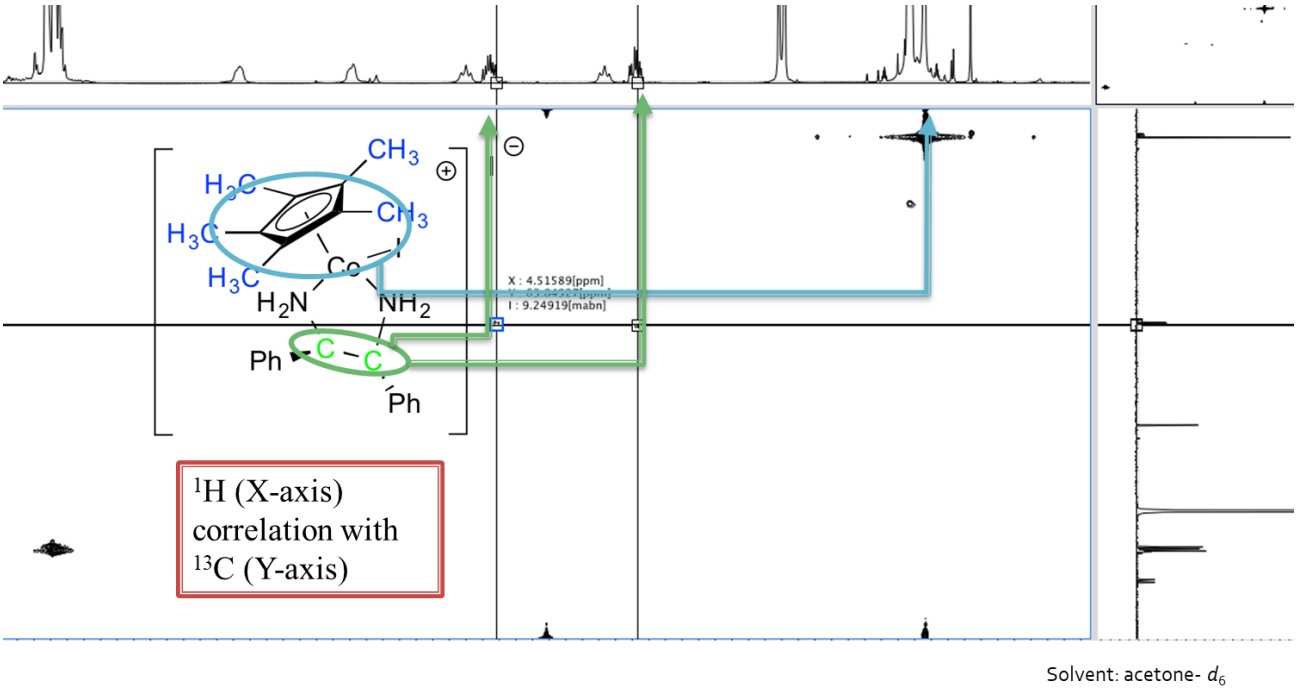
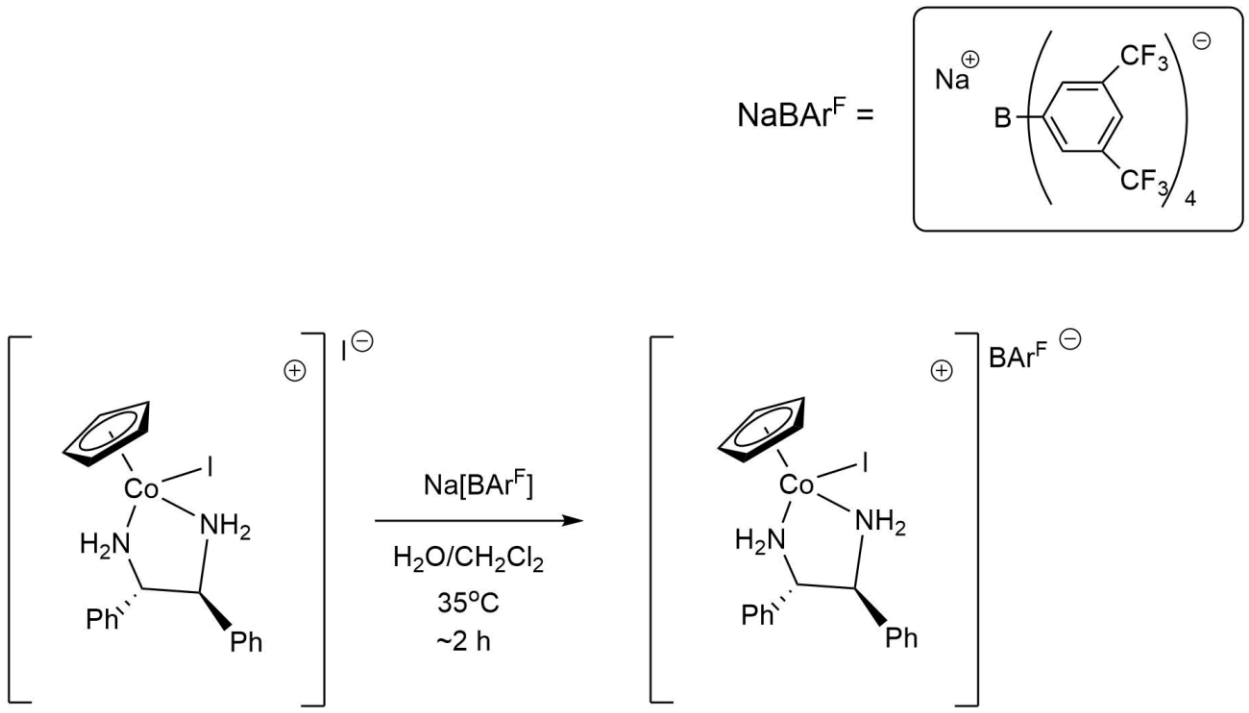
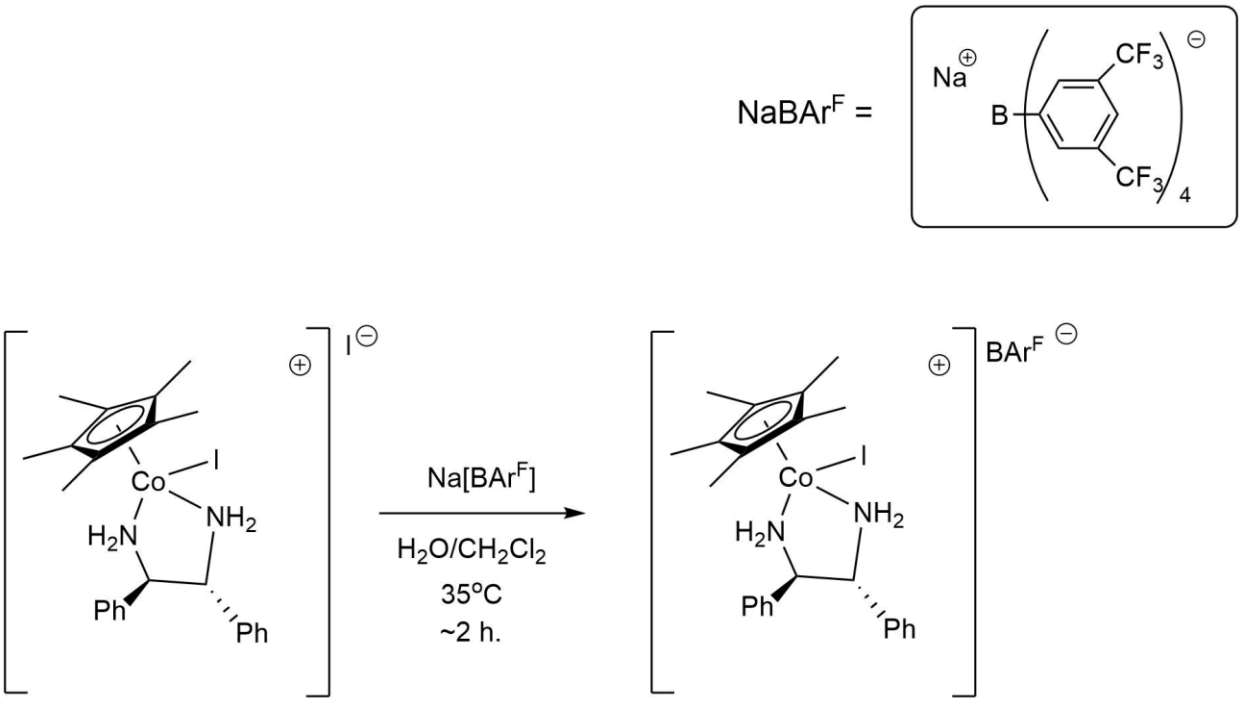


Figure 6. ^{1}H-^{13}C HMQC of [Co(Cp)(R,R-DPEN)(I)](I)*



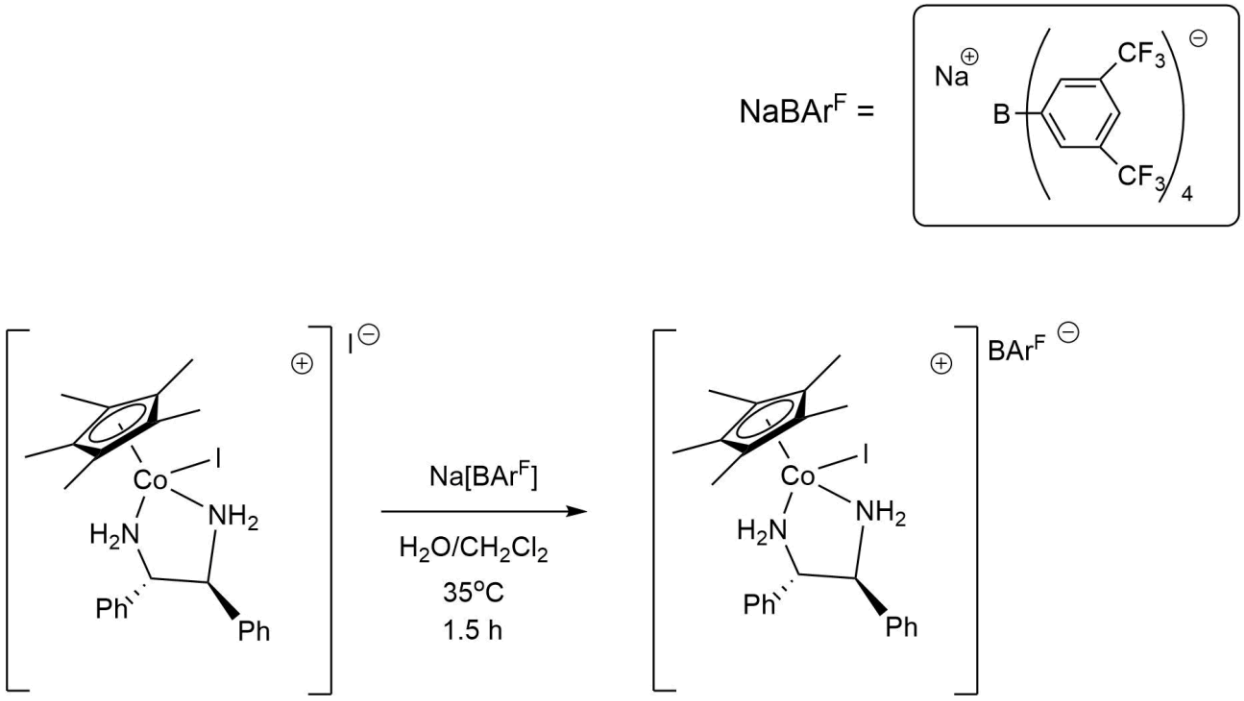
Scheme 4. Synthesis of [Co(Cp)(S,S-DPEN)(I)](BAr^F)

The formation of product [Co(Cp)(S,S-DPEN)(I)](BAr^F) **2a** was confirmed and was analyzed by ^{1}H and ^{13}C NMR. The ^{1}H NMR spectra revealed a singlet at 5.95 ppm, integrating for five protons, which corresponds to the Cp analogue. The two methine groups from the DPEN resonances were revealed at 3.46 ppm and 4.56 ppm as a triplet of doublet. The triplet rises from the CH coupling to the amine protons and the doublet from coupling to one adjacent CH proton. The *ortho* protons on the BAr^F anion appeared at 7.77 ppm as a multiplet. The proton on the *para* position appeared at 7.66 ppm. The ^{13}C NMR spectra revealed a singlet at 85.0 ppm, which corresponds to the Cp analogue. The two methine carbon resonances appeared as multiplets at 64.5 ppm and 66.3 ppm, probably due to mixture of products or free ligand. The *ipso*-Ar resonance appeared as a 1:1:1:1 quartet at 162.5 ppm, due to coupling to boron (I = 3/2). The *ortho* carbon on the BAr^F anion appeared at 130.3 ppm as a quartet, due to coupling to fluorine (I = 1/2).



Scheme 5. Synthesis of [Co(Cp)(R,R-DPEN)(I)](BAr^F)*

The formation of product [Co(Cp*)(R,R-DPEN)(I)](BAr^F) **3a** was confirmed by ^{1}H. The ^{1}H NMR spectra revealed a singlet at 1.94 ppm, integrating for fifteen protons, which corresponds to the Cp* analogue. The two methine groups from the DPEN resonances were revealed at 3.66 ppm and 4.37 ppm as triplet of doublets. The *ortho* protons on the BAr^F appeared at 7.79 ppm as a multiplet and the *para* protons on the BAr^F appeared at 7.67 ppm as a singlet. The BAr^F proton integrations were relatively higher than expected. This is potentially due to excess ligand in the product. The proton on the *para* position appeared at 7.67 ppm. ^{13}C NMR analysis will be explored in the future.



Scheme 6. Synthesis of [Co(Cp)(S,S-DPEN)(I)](BAr^F)*

The formation of product *[Co(Cp*)(S,S-DPEN)(I)](BAr^F)* **4a** was confirmed by ^{1}H NMR. The ^{1}H NMR spectra revealed a singlet at 1.94 ppm, integrating for fifteen protons, which corresponds with the Cp* analogue. The two methine groups from the DPEN resonances were revealed at 3.68 ppm and 4.38 ppm as triplet of doublets. The *ortho* protons on the BAr^F appeared at 7.79 ppm as a multiplet and the *para* protons on the BAr^F appeared at 7.67 ppm as a singlet. The BAr^F proton integrations were relatively higher than expected. This is potentially due to excess ligand in the product. The proton on the *para* position appeared at 7.67 ppm. ^{13}C NMR analysis will be explored in the future.

UV-vis Analysis of [Co(Cp^R)(X,X-DPEN)(I)](I)

UV-Vis Spectroscopy of transition metal complexes experiments are done to quantify electronic transitions of the metal center and the coordinating ligands. UV-Vis experiments were done for products **1**, **2**, **3**, and **4.** Stock solutions of each product of roughly 1.20-1.40 mM in dichloromethane. A summary of the results is listed in *Table 2*. An example spectrum is shown in *Figure 7*.

*Table 2. UV-vis analysis of products **1**, **2**, **3**, and **4***

Complex	Concentration (μM)	λ_{max} (nm)	Abs	ε (L/cm mol)	Transition type
	680	555	0.766	1130	*d-d*
1	57.0	279	1.30	22800	CT or ligand
	690	558	0.888	1290	*d-d*
2	55.2	280	1.37	24800	CT or ligand
	248	565	0.289	1170	*d-d*
3	248	358	1.13	4540	Cp*
	49.6	289	1.29	25900	CT or ligand
	610	565	0.748	1230	*d-d*
4	122	357	0.506	4150	Cp*
	48.8	288	1.20	24600	CT or ligand

For products **1** and **2**, the samples revealed transitions at 279 (**1**), 280 nm (**2**), and 555 (**1**), 558 nm (**2**), with λ_{max} values of 1.30 (**1**), 1.37 (**2**), and 0.766 (**1**), 0.888 (**2**), respectively. The molar absorptivities were calculated to be 22833 (**1**), 24750 L mol^{-1} cm^{-1} (**2**), and 1125 (**1**), 1287 L mol^{-1} cm^{-1} (**2**), respectively. For the 1:2 dilution, there was an unresolved shoulder near 400

nm at 1.40 Abs (**1** and **2**). The transition at 555 (**1**), 558 nm (**2**) is a *d-d* electronic distribution since the transition occurred in the visible region of the spectrum and has a ε value consistent with a *d-d* transition lacking a center of inversion. The transition at 279 (**1**), 280 nm (**2**) indicated a charge transfer between the metal and ligands, or completely ligand based due to the absorption in the UV region of the spectrum and the large magnitude of the ε.

For products **3** and **4**, the samples revealed transitions at 289 (**3**), 288 (**4**), 358 (**3**), 357 (**4**), and 565 (**3**), 565 nm (**4**), with λ_{max} values of 1.29 (**3**), 1.20 (**4**), 1.13 (**3**), 0.506 (**4**), and 0.289 (**3**), 0.748 (**4**) Abs, respectively. The molar absorptivities were calculated to be 25990 (**3**), 24578 (**4**), 4537 (**3**), 4151 (**4**), and 1166 (**3**), 1227 L mol^{-1} cm^{-1} (**4**), respectively. For the 1:5 dilution, there was an unresolved shoulder near 440 nm at 0.300 (**3**), 0.700 Abs (**4**). The transition at 565 (**3**), 565 nm (**4**), is a *d-d* electronic distribution since the transition occurred in the visible region of the spectrum and has a ε value consistent with a *d-d* transition lacking a center of inversion. The transition at 358 (**3**), 357 nm (**4**), could be Cp* based as it is absorbed in the UV region. The transition at 289 (**3**), 288 nm (**4**) indicated a charge transfer between the metal and ligands, or completely ligand based due to the absorption in the UV region of the spectrum and the large magnitude of the ε.

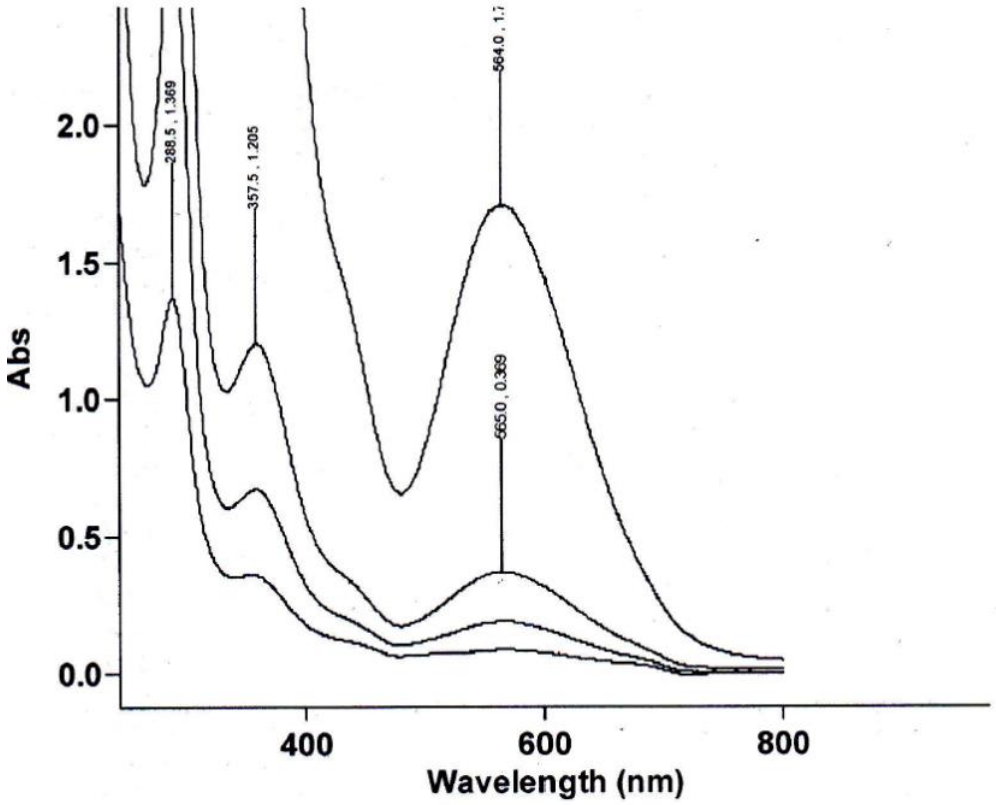


Figure 7. An example UV-vis Spectra of [Co(Cp)(R,R-DPEN)(I)](I)*

X-Ray Crystallography of [Co(Cp^R)(X,X-DPEN)(I)](Y)

Crystal structures were obtained for products **1**, **2a**, and **4** and a summary of the bond lengths and angles are listed in *Table 3.* These are the first single-crystal X-ray structures of Co(III) compounds with both Cp or Cp* ligands and a bidentate amine ligand in its coordination sphere. Among the products obtained, all of them show similar bond lengths and angles. The bond lengths of the Co-N range from 1.965-2.012 Å and the Co-I range from 2.588-2.639 Å.

The bond angles for N1-Co-N2 of all three products show a bite angle between 82-84° while the I-Co-N is 90-95°. These data suggest that the complex is best described as octahedral. It is slightly distorted due to the chelate of the bidentate, making it sterically locked in place at the reduced chelate angle. This steric phenomenon is likely due to the size of the N atom. Indeed,

related Co complexes of the type [Co(Cp*)(P-P)I]I, where P-P is a bidentate phosphine (i.e., the amine small N is replaced by a phosphine large P), have bond angles that are closer to 90°.[13]

Table 3. Crystallography bond distances and angles for [Co(Cp^R)(X,X-DPEN)(I)](Y)

	(**1**)	(**2a**)	(**4**)
Distances (Å)			
Co-I1	2.605(2)	2.5877(10)	2.6388(8)
Co-N1	1.983(7)	1.965(6)	2.012(4)
Co-N2	1.995(8)	2.003(6)	2.008(4)
Angles (°)			
N1-Co-N2	83.7(3)	83.8(2)	82.83(16)
I1-Co-N2	92.1(2)	89.73(19)	94.93(12)
I1-Co-N1	92.1(2)	92.65(18)	89.55(13)

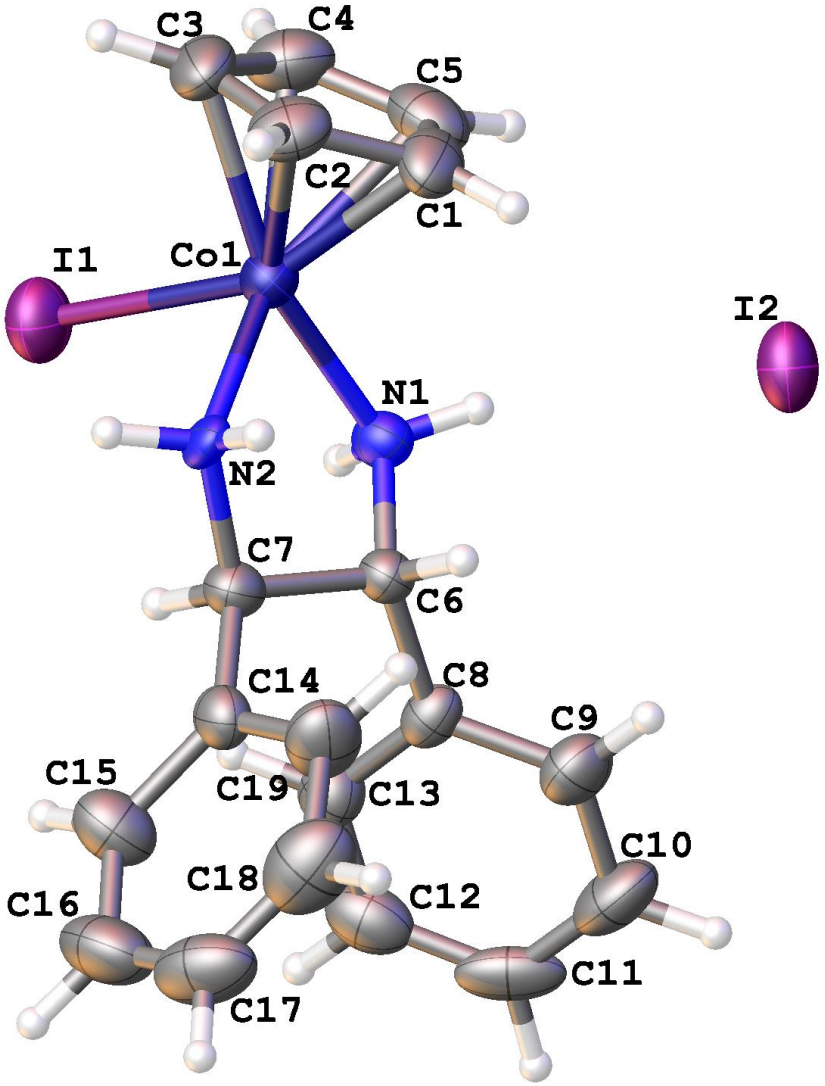


*Figure 8. Crystal of [Co(Cp)(R,R-DPEN)(I)](I) (**1**)*

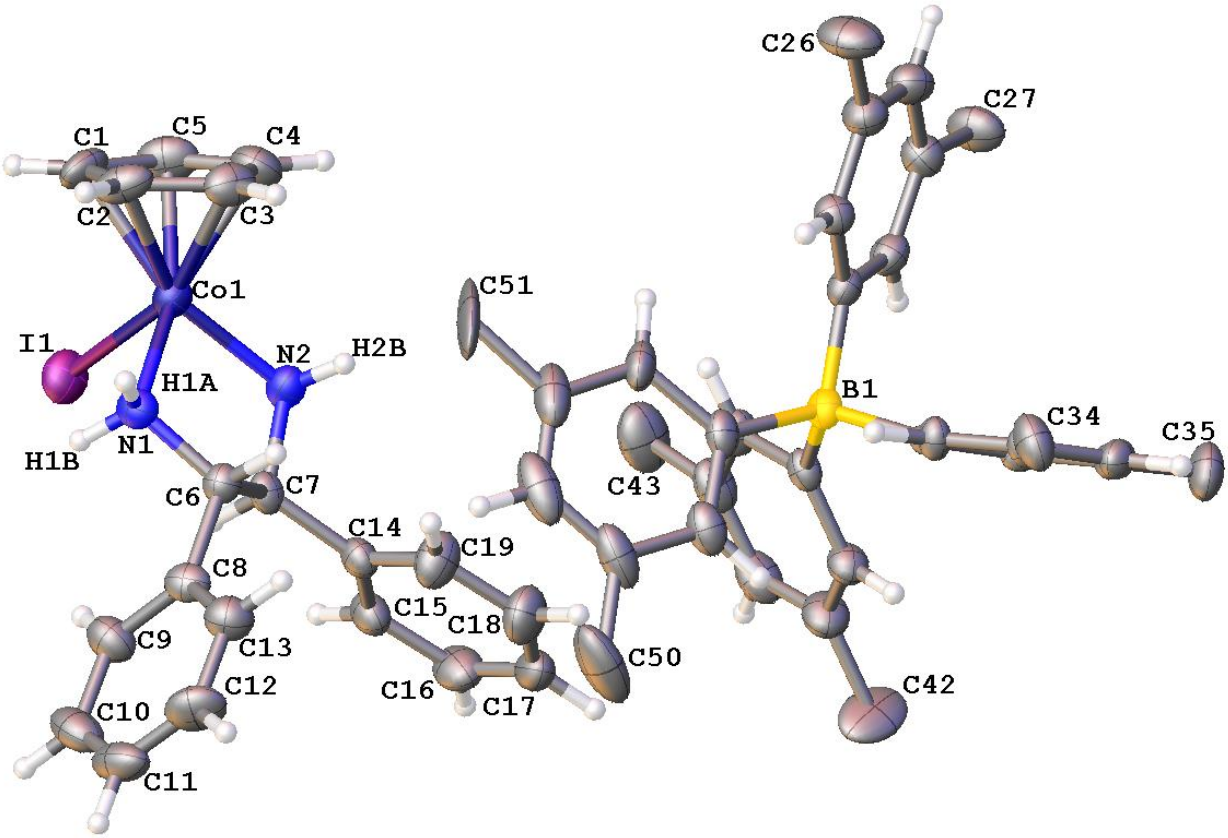


*Figure 9. Crystal of [Co(Cp)(S,S-DPEN)(I)](BAr^F) (**2a**). CF_3 were removed for clarity.*

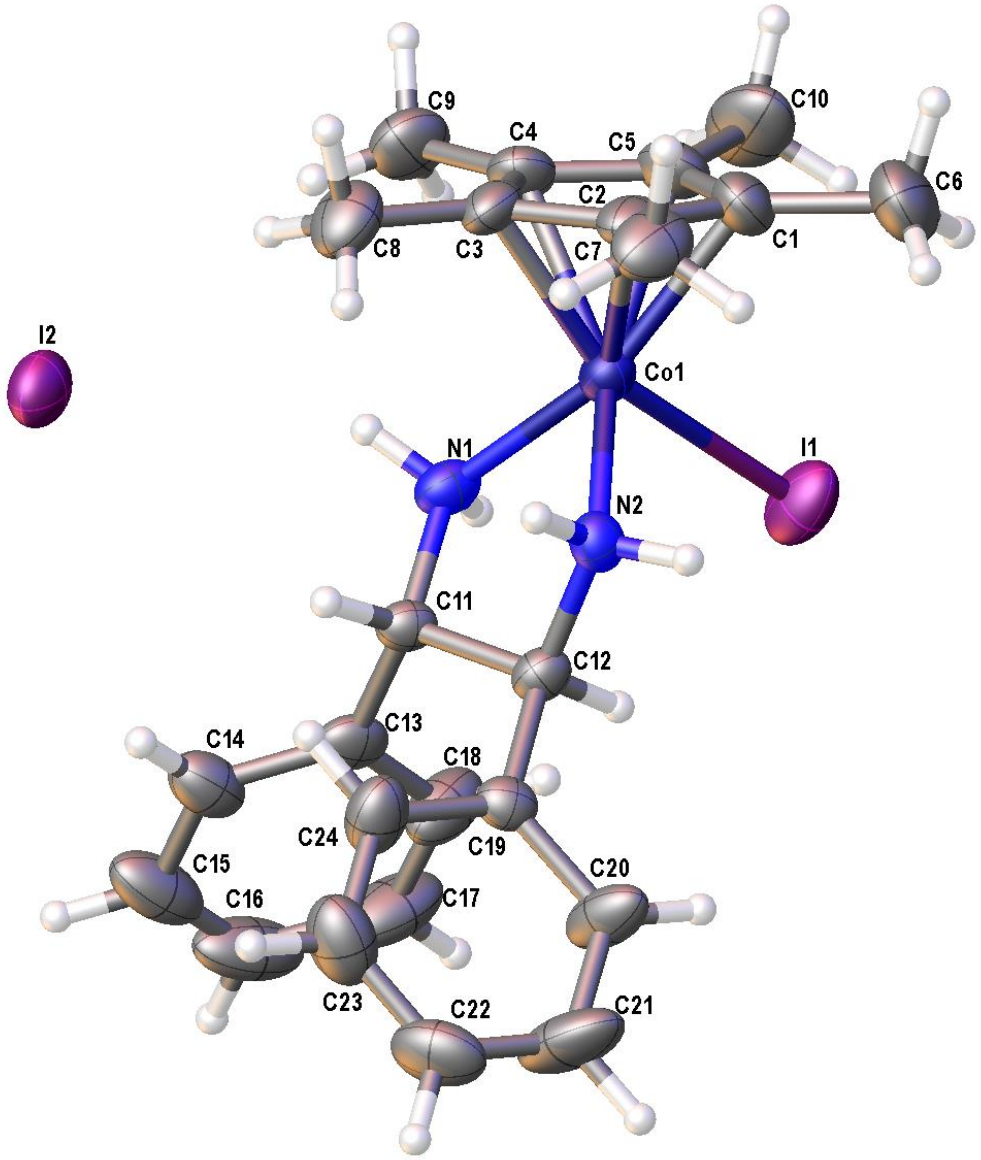
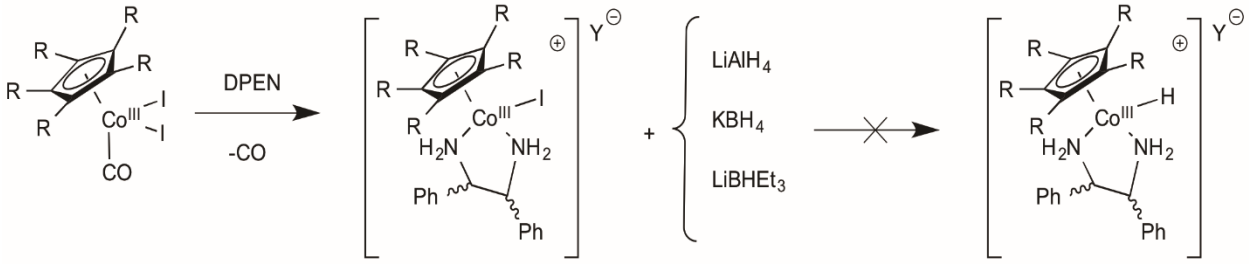


Figure 10. Crystal of [Co(Cp)(S,S-DPEN)(I)](I) (**4**)*

4. Results and Discussion – Part 2 Reactivity

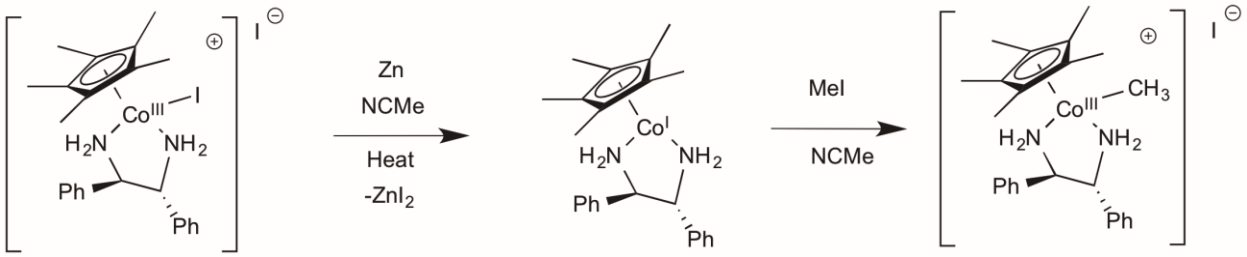
It is important to consider that transition metal hydrides are critical intermediates in homogeneous organometallic catalysis and are involved in multiple catalytic cycles.[14] Rhodium hydride complexes have been synthesized and have been shown to be reactive, making them effective catalysts.[15] Since Rh is in the same periodic group as Co, it was in our interest to explore the possible synthesis and isolation of a Co(III) hydride complex for asymmetric hydrogen transfer reactions. Our initial approach was to use $LiAlH_4$, KBH_4, and $LiBHEt_3$ as hydride donating reagents to add the hydride to the cobalt (*Scheme 7)*. However, these strong reducing agents reduced the metal to Co(II) as indicated by a paramagnetic ^{1}H-NMR spectrum.



Scheme 7. Attempted synthesis of [Co(Cp^R)(X,X-DPEN)(H)](I)

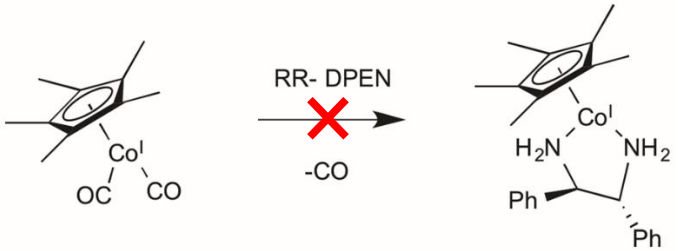
To bypass that route, it was proposed to reduce the complex by 2 e^- and then add a source of electrophilic H^+ or CH_3^+. The source of H^+ to be used was [*p*-bromoanilium]BF_4, which was successfully isolated and has been used before to prepare a Co(III)-H in the complex $[HCo(L2)(CH_3CN)]^{2+}$, where L2 = $P^{nC\text{-}PPh}{}_{22}N^{Ph}{}_2$ (1,5-diphenyl-3,7-bis((diphenylphosphino)alkyl)-1,5-diaza-3,7-diphosphacyclooctane; alkyl = $(CH_2)_2$, *n* = 2 (L2).[10] In initial attempts, CH_3I was used to add an electrophilic methyl group. The reason is due to precedence for oxidative addition to the metal complexes, and the fact that isolating Co(III) with hydrides are rare.[10,16] The reaction proposed is illustrated in *Scheme 8*, where the Co(III)

complex is reduced by Zn to Co(I) and then the addition of CH_3I would oxidize the metal back to a +3 oxidation state. ^{1}H-NMR data showed the Cp* ligand to be absent, and the presence of free DPEN ligand. If the zinc reduced Co(III) to Co(I), the resulting complex likely decomposed (see below).



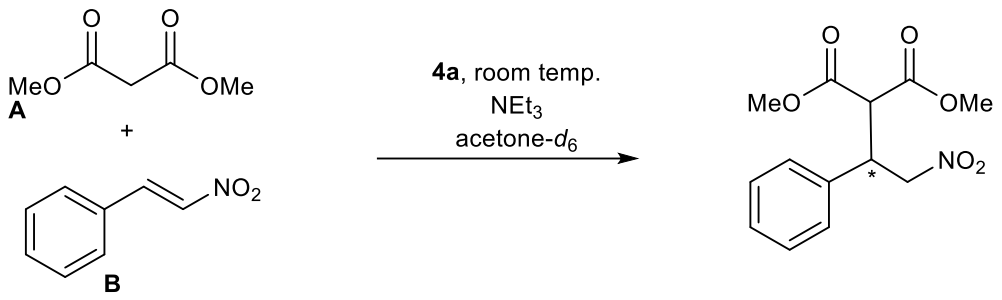
Scheme 8. Attempted synthesis of [Co(Cp)(R,R-DPEN)(CH$_3$)](I)*

The Co(I) complex [Co(Cp*)(CO)$_2$], which is a precursor to the starting point for all previous reactions, could react with DPEN to replace the two carbonyls. However, even in refluxing toluene for 17 h, no reaction was observed as shown by IR spectrum (1931 and 1995 cm^{-1}) which suggests both CO ligands of [Co(Cp*)(CO)$_2$] were still present after the reaction time (*Scheme 9*). Furthermore, this result suggests that if Zn did reduce [Co(Cp*)(R,R-DPEN)(CH$_3$)](I), as described above, the complex likely decomposed at the elevated temperatures.



Scheme 9. Attempted synthesis of [Co(Cp)(R,R-DPEN)]*

Attempts to do a Michael addition



Scheme 10. Attempted Michael Addition of dimethyl malonate and trans-β-nitrostyrene

With the successful synthesis of the BAr^F coordination complexes **2a**, **3a**, and **4a**, we decided to explore its reactivity by attempting the Michael addition reaction. This is a known reaction that is catalyzed by the related $[\Delta/\Lambda\text{-Co(S,S-DPEN)}_3](BAr^F)(Cl)_2$, a cobalt(III) based catalyst.[5] The reaction between dimethyl malonate and *trans*-β-nitrostyrene is catalyzed by $[\Delta/\Lambda\text{-Co(S,S-DPEN)}_3](BAr^F)(Cl)_2$, and due to the similarities to our systems I attempted this reaction with complex **4a**. Although there was a slight color change when the solution was let to sit overnight, the ^{1}H NMR spectrum revealed no observable changes in the chemical shifts. Heating the solution could possibly kinetically initiate the reaction, however, the catalyst was found to decompose at high temperatures.

Anion exchange reactions

A series of outer sphere anion exchange reactions were tested on $[Co(Cp^R)(X,X\text{-DPEN})(I)](I)$ for recrystallization purposes. The anions tested include: sodium tetrafluoroborate ($NaBF_4$), ammonium hexafluorophosphate (NH_4PF_6), sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate ($NaBAr^F$), sodium perchlorate ($NaClO_4$), and silver acetate (AgOAc). Out of the five anions tested, the reaction with $NaBAr^F$ gave the best recrystallization and elemental analysis results, as discussed above. Interestingly, the AgOAc reaction produced an unexpected solubility property.

The complexes became water soluble upon exchanging iodide for acetate, which is significant as this can open up several reactivity pathways in the organic as well as biochemical fields. More details on the acetate complexes will be discussed in Chapter 3.

5. Conclusions and Future Work

Four complexes of the type [Co(Cp^R)(X,X-DPEN)(I)](I) have been synthesized. The related meso complexes show a mixture of two diastereomers that appears to be dependent on sterics. All four of the enantiomerically pure complexes have been fully characterized by $^1H/^{13}C$ NMR, Low-Res MS, UV-Vis, elemental analysis, and, for three complexes, single-crystal X-ray diffraction. Attempts were made to prepare a Co(III)-H complex via direct hydride/iodide ligand exchange as well as 2-e^- reduction followed by an oxidative addition. However, the reduction was unsuccessful, suggesting that the DPEN ligand addition solely favors Co(III) complexes. Conditions were found for outer-sphere anion exchange; where exchange for the BAr^F anion results in crystalline material that produces publishable elemental analysis results and with the OAc anion results in water soluble complexes**.** The next step will be exploring the reactivity of the complex with *cis*-1,2-diaminocyclohexane (DIAC). This ligand will serve as an electron donating system to the complex, which can help mediate the net positive charge to result in a more covalent system that can potentially provide better access to a Co(III)-H complex.

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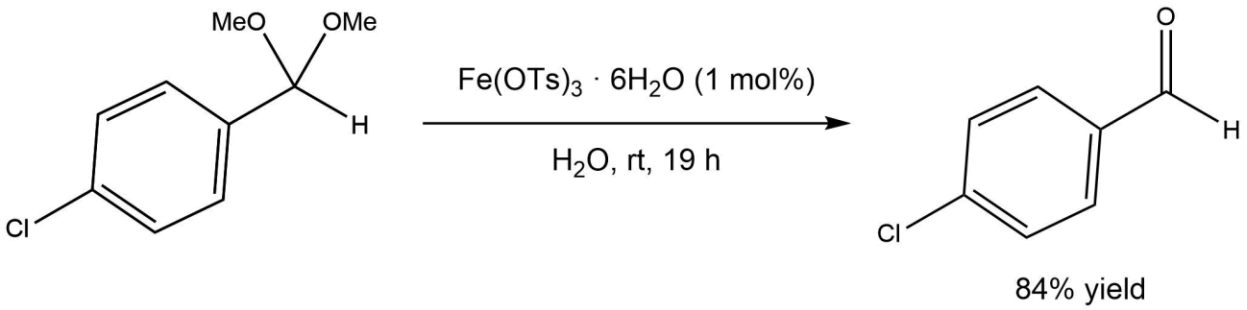
Chapter 3: Exploration of aqueous Co(III) acetate complexes for catalytic activity

1. Introduction

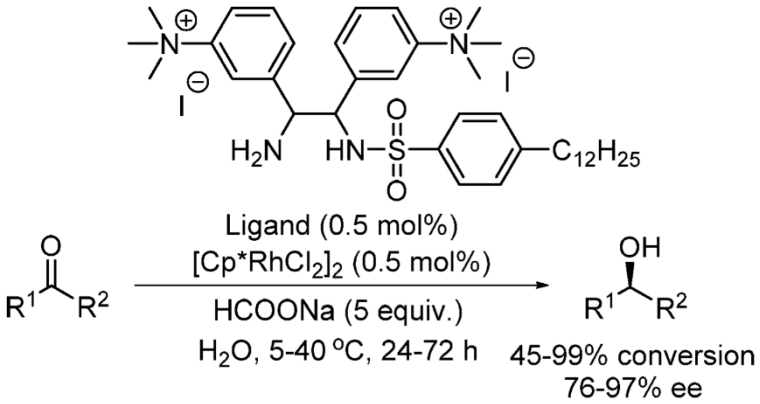
There is a growing interest in green synthetic methodology among researchers in academic and industrial fields focusing on eliminating chlorinated solvents.[1] As a result, alternative solvents have been developed to combat environmental concerns.[2] Of these, water is an ideal solvent for synthesis due to its availability, cost, nonflammability, environmental congruity, and nontoxicity. Recently, there has been a growing interest in aqueous organometallic catalysis, a field that takes advantage of this green solvent[3]



Scheme 1. Fe(III) Tosylate-Catalyzed Deprotection of Aromatic acetals in water

Specific examples of organometallic reactions that take advantage of water as a solvent, specifically utilizing rare earth metals, include the addition of H_2 to trans-$Ru(P_2)_2Cl_2$ (P_2 = a bidentate phosphine) to form trans-$[Ru(P_2)_2(H_2)H]^+$ dihydrogen complexes. Another example is the molybdocene-catalyzed hydration of nitriles.[4,5] Generally, metal chlorides, perchlorates, and other species that contain first row transition metals, Ni, Fe, Cu, and Zn, exhibit high catalytic activity due to optimal Lewis acid characteristics in aqueous media.[2] This Lewis acid feature is dependent on the hydrolysis constants (pK_h) as well as water exchange rate constants (WERCs).[6] The WERC is a significant factor of Lewis acid strength in aqueous catalysis.[2] As the value of WERC increases, the catalytic activity increases. An example of aqueous catalytic reactions include an Fe(III) tosylate-catalyzed (tosylate = 4-toluenesulfonate) deprotection of aromatic

acetals in water, where the acetals were deprotected in the presence of Fe(III) tosylate under mild conditions (*Scheme 1*).[7]



Scheme 2. Asymmetric Transfer Hydrogenation by a Surfactant-Type Rh Catalyst in Water.[2]

There have been several reports of transfer hydrogenation in aqueous conditions using transition metals. A surfactant type Rh complex successfully catalyzed a transfer hydrogenation of ketones in water with 94% yield and with 84% ee (*Scheme 2*).[2,8] This surfactant system showed high activity on a variety of aliphatic ketones with functional groups that might be formed into intermediates of anticoagulants.

Another example of a successful catalyzed transfer hydrogenation of ketones using Rh was demonstrated by Himeda *et al.*[3] Their group utilized achiral [Cp*Rh(bpy)Cl]Cl,

Figure 1. Acetate complex soluble in aqueous phase

[Cp*Ir(bpy)Cl]Cl, and [(C_6Me_6)Ru(bpy)Cl]Cl (C_6Me_6 = hexamethylbenzene) complexes with aqueous formic acid and sodium formate as a hydrogen source, resulting in a 89-99% yield of 1-phenylethanol. Also, Thorpe et al. prepared Rh and Ir complexes using aminosulfonamide ligands [Ts-DPEN and *N*-(*p*-toluenesulfonyl)-cyclohexanediamine] and [Cp*MCl_2]$_2$ (M = Rh, Ir), in 51% water to catalyze transfer hydrogenation of ketones (*Scheme 3*).[9]

As mentioned in Chapter 2, our group conducted a series of outer anion exchange reactions on [Co(Cp^R)(X,X-DPEN)(I)](I) for recrystallization purposes. Out of the five anions experimented, the reaction using silver acetate (AgOAc) produced an unanticipated water-soluble product [Co(Cp)(S,S-DPEN)(OH_2)]($OAc)_2 \cdot n H_2O$] (**8**) (*Figure 1*). This is interesting as our complexes are not typically water soluble. Nonetheless, since aqueous catalysis has been known and experimented on with organometallic transition metal complexes, it was in our interest to explore the synthesis and reactivity of this new product. In this chapter, the synthesis and characterization of seven new acetate complexes will be discussed. Also, the reactivity of these complexes will be analyzed, specifically if they were able to catalyze transfer hydrogenation of ketones using water and sodium formate and/or a mixture of formic acid and triethylamine.

2. Experimental Section

2.1. Materials

All solvents and reagents were used as received. The ligands R,R-DPEN, S,S-DPEN, as well as both silver acetate (AgOAc) and cesium acetate (CsOAc) were purchased from either Aldrich Chemical Company or Alfa Aesar and used as received. The metal reagents [Co(Cp)(CO)$(I)_2$] and [Co(Cp*)(CO)$(I)_2$] were prepared as previously reported.[10,11]

2.2. Measurements

^{1}H and ^{13}C NMR spectra were obtained on a JEOL ECX 400 MHz spectrometer (operating frequency for ^{13}C NMR was 100 MHz) and referenced against tetramethylsilane using residual proton signals (^{1}H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). Elemental analyses were performed by Atlantic Microlab, Inc in Norcross, GA.

2.3.Syntheses

*2.3.1. Preparation of [Co(Cp)(R,R-DPEN)(OH_2)](OAc)$_2$ · nH_2O (**7**).*

A 100 mL beaker was charged with **1** (0.0806 g, 0.0137 mmol) and dichloromethane (10 mL), silver acetate (0.0692 g, 0.415 mmol), and H_2O (10 mL). Immediately, the aqueous layer began to turn bright purple/pink. The solution was vigorously stirred for 10 min at room temperature. The aqueous layer was collected and filtered. The filter paper was washed with water. The resultant filtrate was dried in the fume hood, leaving a light purple solid. The final product weighed 0.0195 g. ^{1}H NMR (39a-1H-LD-5), ^{13}C NMR (39a-13C-LD).
^{1}H NMR ($CDCl_3$, δ): 6.92-7.24 (12H, m, DPEN aromatic and NH), 5.84 (5H, s, Cp), 5.01 (1H, td, CH), 4.63 (1H, d, NH), 3.98 (1H, td, CH), 2.22-2.28 (2H, m, OH_2), 2.20 (6H, s, OAc). ^{13}C {^{1}H} NMR ($CDCl_3$, δ): 182 (1C, s, C=O), 138.2 (1C, s, ipso *C* arene), 136.7 (1C, s, ipso *C* arene) 129.3, 129.2, 129.1, 128.8, 128.8, 128.6, 128.4, 128.0, 127.9, 127.2 (10C, m, Aromatic *C* DPEN), 84.4 (5C, s, *Cp*), 64.1 (1C, s, DPEN CH), 62.4 (1C, s, DPEN CH), 24.7 (1C, s, OAc CH_3). Anal. Calcd for $C_{21}H_{26}O_3N_2CoI$: C, 46.7; N, 5.19; H, 5.93. Found: C, 46.4; N, 5.53; H, 4.73, I, 20.8.

*2.3.2. Preparation of [Co(Cp)(S,S-DPEN)(OH_2)](OAc)$_2$ · nH_2O (**8**).*

A 50 mL round-bottom flask was charged with **2** (0.100 g, 0.170 mmol) and dichloromethane (10 mL), silver acetate (0.0568 g, 0.340 mmol), and H_2O (10 mL). Immediately, the aqueous

layer began to turn bright purple/pink. The solution was vigorously stirred for 10 min at room temperature. The aqueous layer was collected and filtered. The filter paper was washed with water. The resultant filtrate was transferred into a round-bottom flask and was dried *in vacuo*, leaving a light purple solid. *Note: Extensive foaming and bumping occurred during solvent removal.* The final product weighed 0.0626 g. ^{1}H NMR (50b-1H-LD), ^{13}C NMR (50a-13C-LD). ^{1}H NMR ($CDCl_3$, δ): 6.88-7.35 (12H, m, DPEN aromatic and NH), 6.02 (5H, s, Cp), 5.04 (1H, td, CH), 4.65 (1H, d, NH), 4.04 (1H, td, CH), 2.22-2.33 (3H, m, OH_2), 2.21 (6H, s, OAc). ^{13}C {^{1}H} NMR ($CDCl_3$, δ): 182 (1C, s, C=O), 137.9 (1C, s, ipso *C* arene), 136.4 (1C, s, ipso *C* arene) 129.5, 129.3, 129.2, 128.9, 128.8, 128.7, 128.3, 128.2, 127.6, 127.2 (10C, m, Aromatic *C* DPEN), 84.5 (5C, s, *Cp*), 64.0 (1C, s, DPEN CH), 62.7 (1C, s, DPEN CH), 24.6 (1C, s, OAc CH_3). Anal. Calcd for $C_{27}H_{39}N_2Co$: N, 6.14; H, 5.93. Found: N, 6.14; H, 5.93. Anal. Calcd for $C_{21}H_{26}O_3N2CoI$: C, 58.47; N, 5.93; H, 6.14. Found: C, 57.94, N, 5.93; H, 6.14.

2.3.3. Preparation of [Co(Cp)(R,R-DPEN)(OH_2)]$(OAc)_2 \cdot n H_2O$ (**9**).*

A 50 mL round-bottom flask was charged with **3** (0.1001 g, 0.1516 mmol) and dichloromethane (10 mL), silver acetate (0.0506 g, 0.3032 mmol), and H_2O (10 mL). Immediately, the aqueous layer began to turn bright purple/pink. The solution was vigorously stirred for 10 min at room temperature. The aqueous layer was collected and filtered. The filter paper was washed with water. The resultant filtrate was transferred into a round-bottom flask and was dried *in vacuo*, leaving a light purple solid. *Note: Extensive foaming and bumping occurred during solvent removal.* The final product weighed 0.0611 g. ^{1}H NMR (51b-1H-LD), ^{13}C NMR (51a-13C-LD). ^{1}H NMR ($CDCl_3$, δ): 7.02-7.30 (12H, m, DPEN aromatic and NH), 6.34 (1H, t, NH), 5.58 (1H, td, CH), 5.00 (1H, t, NH), 4.90 (1H, t, NH), 4.58 (1H, td, CH), 2.23 (5H, s, OAc), 1.99 (4H, m, OH_2), 1.56 (15H, s, Cp*). ^{13}C {^{1}H} NMR ($CDCl_3$, δ): 181.87 (1C, s, C=O), 138.5 (1C, s, ipso *C*

arene), 137.0 (1C, s, ipso *C* arene) 128.9, 128.8, 128.7, 128.5, 128.4, 128.4, 128.3, 127.5, 127.3, 127.2 (10C, m, Aromatic *C* DPEN), 92.3 (5C, s, *Cp*), 63.2 (1C, s, DPEN CH), 61.2 (1C, s, DPEN CH), 24.5 (1C, s, OAc CH_3), 9.43 (5C, s, Cp* CH_3). Anal. Calcd for $C_{21}H_{26}O_3N_2CoI$: C, 46.7; N, 5.19; H, 5.93. Found: C, 46.4; N, 5.53; H, 4.73, I, 20.8.

2.3.4. Preparation of [Co(Cp)(S,S-DPEN)(OH_2)]$(OAc)_2 \cdot n H_2O$ (**10**).*

A 50 mL round-bottom flask was charged with **4** (0.0300 g, 0.0454 mmol) and dichloromethane (10 mL), silver acetate (0.0506 g, 0.102 mmol), and H_2O (10 mL). Immediately, the aqueous layer began to turn bright purple/pink. The solution was vigorously stirred for 30 min at room temperature. The aqueous layer was collected and filtered. The filter paper was washed with water. The resultant filtrate was evaporated in the fume hood, leaving a light purple solid. The final product weighed 0.0200 g. ^{1}H NMR (68a-1H-LD-5), ^{13}C NMR (68a-13C-LD).

^{1}H NMR ($CDCl_3$, δ): 7.00-7.38 (12H, m, DPEN aromatic and NH), 6.27 (1H, t, NH), 4.88 (1H, td, CH), 4.77 (1H, d, NH), 4.53 (1H, td, CH), 3.07 (6H, s, OAc), 2.22 (6H, s, OAc), 1.91 (3H, m, OH_2), 1.51 (15H, s, Cp*). ^{13}C {^{1}H} NMR ($CDCl_3$, δ): 182 (1C, s, C=O), 138.7 (1C, s, ipso *C* arene), 137.2 (1C, s, ipso *C* arene), 129.1, 128.9, 128.8, 128.6, 128.5, 128.3, 128.3, 128.1, 127.5, 127.1 (10C, m, Aromatic *C* DPEN), 92.3 (5C, s, *Cp*), 63.2 (1C, s, DPEN CH), 60.9 (1C, s, DPEN CH), 26.7 (1C, s, OAc CH_3), 9.38 (5C, s, Cp* CH_3).

2.3.5. Preparation of [Co(Cp)(R,R-DPEN)(OAc)](OAc) $\cdot n H_2O$ (**11**).*

A 50 mL round-bottom flask was charged with [Co(Cp*)$(CO)(I)_2$] (0.2500 g, 0.525 mmol), dichloromethane (25 mL), followed by silver acetate (0.175 g, 1.05 mmol). The solution was vigorously stirred for 30 min at room temperature. After the 30 min, the solution appeared bright blue. The round-bottom was then charged with R,R-DPEN (0.1675

g, 0.789 mmol). The solution immediately turned bright purple upon stirring. The solution remained stirring for 30 min. The solution was then transferred to an evaporating dish. The dried product was then washed with hexanes. The final product weighed 0.284 g. ^{1}H NMR (74a-1H-LD), ^{13}C NMR (74b-13C-LD).

^{1}H NMR ($CDCl_3$, δ): 6.96-7.36 (16H, m, DPEN aromatic and NH), 6.43 (1H, t, NH), 5.68 (1H, t, NH), 4.94 (1H, m, CH), 4.58 (1H, td, CH), 2.79 (7H, s, OAc/H_2O) 2.23 (5H, s, OAc/H_2O), 1.92 (4H, s, OAc/H_2O), 1.55 (15H, s, Cp*) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$, δ): 182 (1C, s, C=O), 138.8 (1C, s, ipso *C* arene), 137.2 (1C, s, ipso *C* arene), 129.3, 128.9, 128.8, 128.6, 128.4, 128.3, 127.5, 127.2, 127.0, 126.60 (10C, m, Aromatic *C* DPEN), 92.3 (5C, s, *Cp*), 63.2 (1C, s, DPEN CH), 60.9 (1C, s, DPEN CH), 26.7 (1C, s, OAc CH_3), 9.42 (15C, s, *Cp**) ppm.

2.3.6. Preparation of [Co(Cp)(R,R-DPEN)(OAc)](I) · nH_2O (**12**).*

A 50 mL round-bottom flask was charged with [Co(Cp*)(CO)$(I)_2$] (0.2503 g, 0.526 mmol), dichloromethane (15 mL), followed by cesium acetate (0.094 g, 0.490 mmol). The solution was vigorously stirred for 30 min at room temperature. After the 30 min, there were no observable color changes. The cesium acetate was still visible as yellow clumps. The round-bottom was then charged with R,R-DPEN (0.1674 g, 0.789 mmol). The solution began to gradually turn a brighter purple upon stirring. The yellow CsOAc clumps turned white, indicating a possible change into CsI. The solution remained stirring for 30 min. The solution was then filtered through celite and then transferred to an evaporating dish. The dried product was then washed with hexanes. The final product weighed 0.358 g. ^{1}H NMR (80a-1H-LD), ^{1}H NMR ($CDCl_3$, δ): 6.99-7.52 (14H, m, DPEN aromatic and NH), 5.57 (2H, m, NH), 4.89 (2H, m, NH;CH), 4.53 (1H, td, CH), 2.26 (1H, m, OH_2), 2.23 (6H, s, OAc), 2.17 (3H, m, OH_2), 1.96 (6H, s, OAc), 1.53 (15H, s, Cp*).

2.3.7. Preparation of [Co(Cp)(S,S-DPEN)(OAc)](I) · 3H_2O (**13**).*

A 50 mL round-bottom flask was charged with **4** (0.0400 g, 0.0606 mmol) and dichloromethane (10 mL), cesium acetate (0.0463 g, 0.241 mmol), and H_2O (2 mL). Immediately, the aqueous layer began to turn bright purple/pink. The solution was vigorously stirred for 1 h 30 min at room temperature. The aqueous layer was collected and filtered. The filter paper was washed with water. The resultant filtrate was evaporated in the fume hood, leaving a light purple solid. No recorded yield. ^{1}H NMR (63a-1H-LD-5), ^{13}C NMR (63a-13C-LD).

^{1}H NMR ($CDCl_3$, δ): 7.08-7.37 (13H, m, DPEN aromatic and NH), 5.57 (2H, m, NH), 4.98 (1H, td, CH), 4.40 (2H, m, NH;CH), 2.33 (1H, m, OH_2), 2.24 (3H, s, OAc), 2.22 (1H, s, OH_2), 1.81 (9H, m, OH_2 and OAc), 1.66 (2H, m, OH_2), 1.62 (15H, s, Cp*). ^{13}C {^{1}H} NMR ($CDCl_3$, δ): 181.87 (1C, s, C=O), 137.7 (1C, s, ipso *C* arene), 133.7 (1C, s, ipso *C* arene) 129.4, 129.3, 129.2, 129.1, 128.8, 128.2, 128.1, 128.0, 127.5, 127.2 (10C, m, Aromatic *C* DPEN), 93.0 (5C, s, *Cp*), 63.5 (1C, s, DPEN CH), 62.4 (1C, s, DPEN CH), 26.5 (1C, s, OAc CH_3), 10.7 (5C, s, Cp* CH_3). NMR data revealed a mixture of products.

2.3.8. VT ^{1}H NMR of [Co(Cp)(S,S-DPEN)(OH_2)]($OAc)_2$ (**10**)*

A sample of **10** was dissolved $CDCl_3$ and was first heated from room temperature in 10˚ increments to 55 ˚C in 10 ˚C increments. Peaks at 3.05, 2.20, and 1.92 ppm coalesced at 55 ˚C. Afterwards, the sample was cooled incrementally 55 ˚C to -40 ˚C. No significant changes occurred during cooling. (68a-h-1H-LD).

2.3.9. VT ^{1}H NMR of [Co(Cp)(R,R-DPEN)(OAc)](OAc) (**11**).*

A sample of **11** was dissolved $CDCl_3$ and was first cooled from room temperature in increments leading down to -20 °C in 10 °C increments. No significant changes occurred during cooling. Afterwards, the sample was heated incrementally from -20 °C to 45 °C in 10 °C increments. Peaks at 2.20 and 1.92 coalesced at 45 °C. (76a-f-1H-LD).

2.3.10. Attempt 1 of Transfer Hydrogenation of Acetophenone

A 5 mL round-bottom flask was charged with **7** (0.0105 g, 0.0201 mmol), H_2O (3 mL), sodium formate (0.695 g, 10.2 mmol), and acetophenone (0.24 mL, 2.06 mmol). The dark purple solution was mixed at 75 °C for 21 h. After stirring, two layers were formed. The lower aqueous phase appeared a hazy-beige color, while the upper organic phase appeared dark brown. It appeared that the sodium formate precipitated in between the phases. The organic layer was extracted with diethyl ether. It was filtered via gravity filtration and was then transferred into an evaporating dish. After the volatiles were evaporated, the dried product was analyzed via ^{1}H NMR. There is no indication that 1-phenylethanol was present in the product.

2.3.11. Attempt 2 of Transfer Hydrogenation of Acetophenone

A 5 mL round-bottom flask was charged with **7** (0.0100 g, 0.0191 mmol), D_2O (2 mL), sodium formate (0.6517 g, 9.58 mmol), and acetophenone (0.24 mL, 2.06 mmol). The reactants were mixed starting at 45 °C and then constant at 50 °C for about 2 h. The initial solution color was dark purple. After 1 h, a color changed occurred. The bottom aqueous layer turned light pink and the top organic layer turned brown. A 5 mL sample was taken from the aqueous layer for ^{1}H NMR analysis. The data revealed a large acetophenone peak. The remaining solution continued to react at 80 °C for another 1 h. A ^{1}H NMR sample was taken in DMSO-*d*6 to check for evidence of 1-phenylethanol. There was no indication of expected product.

2.3.12. Attempt 3 of Transfer Hydrogenation of Acetophenone

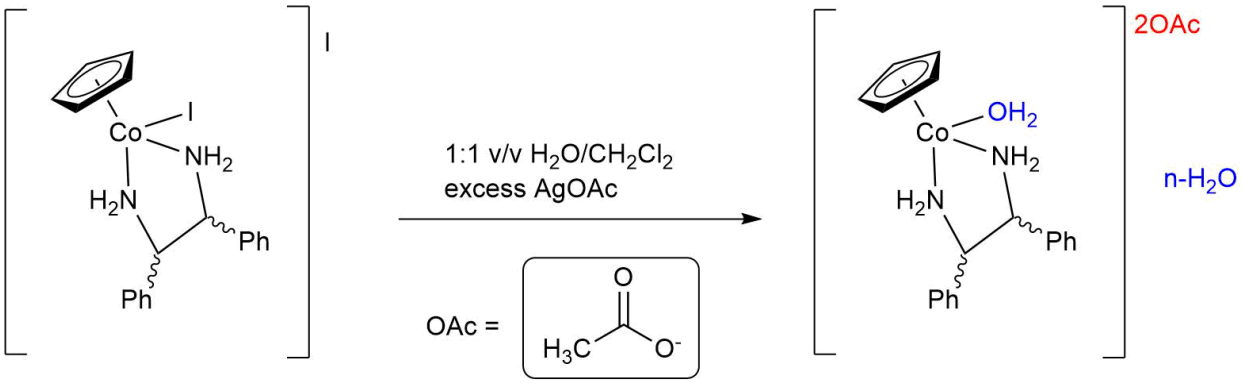
A 5 mL round-bottom flask was charged with formic acid (0.82 mL) and triethylamine (1.2 mL). The flask was then charged with acetophenone (0.25 mL, 2.14 mmol), and **9** (0.0139 g, 0.0235 mmol). The bright purple solution was stirred for about 3 h at 40 °C. The product was isolated by solvent removal via diethyl ether extraction followed by diethyl ether removal *in vacuo*. A viscous liquid (acetophenone and other organic product) was left over. A ^{1}H NMR sample was taken and revealed no indication of 1-phenylethanol.

2.6. X-Ray Crystallography Data Collection and Processing

Appendix A contains crystal data, collection parameters, and refinement criteria for the crystal structure of **13**. The crystal was grown by slow evaporation from a dichloromethane solution. The crystal was mounted on the tip of a Bruker SPINE-pin mount and X-ray intensity data were measured at low temperature using an Oxford Cryosystems Desktop Cooler (200(2) K) for the structure with a graphite monochromated Mo kα radiation (λ = 0.71073 Å) on a Bruker SMART X2S Benchtop diffractometer. Integration, data reduction and scaling were carried out with the programs SAINT and SADABS in the Bruker APEX2 suite of software. The structure was solved (XS) using direct methods and refined using full matrix least squares refinement (SHELXL2017) within Olex2. A direct-methods solution was calculated that provided the non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All of the hydrogen atoms in the structure was placed in ideal positions and refined as riding atoms.

3. Results and Discussion – Part 1 Synthesis and Characterization

Synthesis of [Co(Cp)(X,X -DPEN)(OH_2)]($OAc)_2$ · nH_2O (**7**,**8**)



Scheme 4. Synthesis of [Co(Cp)(X,X-DPEN)(OH_2)]($OAc)_2$ · nH_2O

During the anion exchange experiments mentioned Chapter 2, a water soluble complex of the type [Co(Cp)(X,X-DPEN)(OH_2)]($OAc)_2$ · nH_2O was synthesized. These products can be obtained by reacting [Co(Cp^R)(X,X-DPEN)(I)](I) with AgOAc in a water/dichloromethane solvent mixture. Complexes [Co(Cp)(R,R-DPEN)(OH_2)]($OAc)_2$ · nH_2O **7** and [Co(Cp)(S,S-DPEN)(OH_2)]($OAc)_2$ · nH_2O **8** were confirmed by ^1H and ^{13}C NMR. The ^1H NMR spectra revealed a singlet at 5.84 (**7**), 6.02 ppm (**8**), respectively, corresponding to the five protons on the the Cp ligand. The two methine protons from the DPEN resonances are chemically different due to the lack of a mirror plane and resonate at 5.01 (**7**), 5.04 ppm (**8**) and 3.98 (**7**), 4.04 ppm (**8**) as triplet of doublets. The triplet rises from the CH coupling to the amine protons and the doublet from coupling to one adjacent CH proton. The two OAc resonances appeared as singlets at 2.20 (**7**), 2.22 ppm (**8**). The ^{13}C NMR spectra revealed a singlet at 84.4 (**7**), 84.5 ppm (**8**), which corresponds with the Cp ligand. The resonances for the two methines on the DPEN appeared at

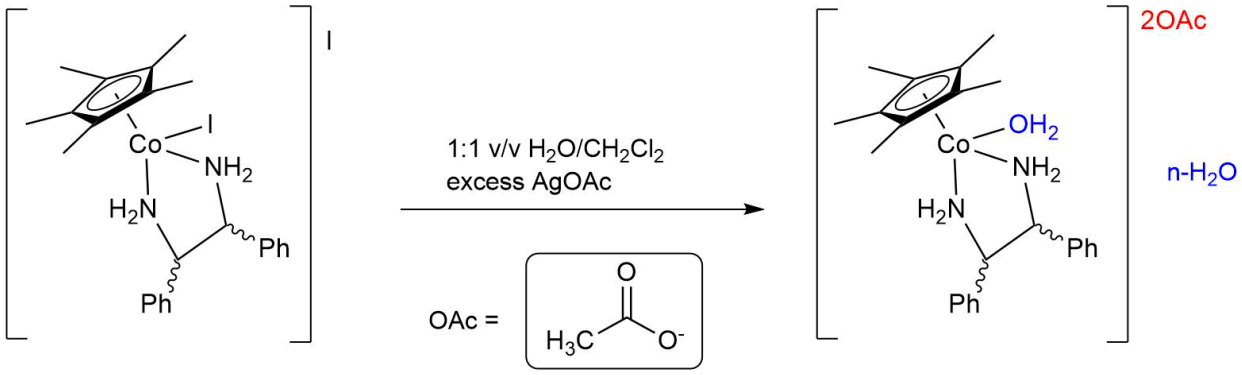
64.1 and 62.4 (**7**), 64.0 and 62.7 ppm (**8**), and 62.4 (**7**), 62.7 ppm (**8**), as singlets. The OAc peaks were revealed as singlet at 24.7 (**7**), and 24.6 ppm (**8**).

Table 1. Elemental analysis data for [Co(Cp)(X,X -DPEN)(OH_2)]($OAc)_2 \cdot n H_2O$

Elemental Analysis		
	Calculated	**Found**
7	C: 46.7	C: 46.4
	H: 5.93	H: 4.73
	N: 5.19	N: 5.53
	I: 0	I: 20.8
8	C: 58.47	C: 57.94
	H: 6.14	H: 6.14
	N: 5.93	N: 5.93
	I: 0	I: 0

In *Table 1*, elemental analysis data are summarized. For compound **7**, it is evident that one I is removed and for **8**, both I are removed. This conflicting data will be further explored in order to understand the nature of these reactions. Although the reaction procedures were similar, there could possibly be a stoichiometry factor that influences the removal of the I. As these structures are similar to **9** and **10**, which will be discussed later, there could be a mixture of hydrate isomers in these products where the I, OH_2, and OAc coordination are interchangeable between the inner sphere and outersphere in solution.

Synthesis of [Co(Cp*)(X,X -DPEN)(OH_2)]($OAc)_2$ · nH_2O (**9**,**10**)



Scheme 5. Synthesis of [Co(Cp)(X,X-DPEN)(OH_2)]($OAc)_2$ · nH_2O*

Complexes [Co(Cp*)(R,R-DPEN)(OH_2)]($OAc)_2$ · nH_2O **9** and [Co(Cp)(S,S-DPEN)(OH_2)]($OAc)_2$ · nH_2O **10** were confirmed by ^{1}H, VT-^{1}H, ^{13}C NMR, and ^{1}H-^{13}C HMQC NMR spectroscopy. The ^{1}H NMR spectra revealed a singlet at 1.56 (**9**), 1.51 ppm (**10**), integrating for fifteen protons, which corresponds with the methyl groups on the Cp*. The two methine protons from the DPEN resonances were revealed As triplet of doublets at 5.58 (**9**), 4.88 ppm (**10**) and 4.58 (**9**), 4.53 ppm (**10**). The triplet rises from the CH coupling to the amine protons and the doublet from coupling to one adjacent CH proton. The OAc resonance appeared as a singlet at 2.23 (**9**) and 2.22 ppm (**10**). The ^{13}C NMR spectra revealed a singlet at 92.3 (**9**), 92.3 ppm (**10**), which corresponds with the Cp* aromatic ring. Two methine carbon resonances appeared at 63.7 and 65.0 (**9**), and 64.2 and 64.6 ppm (**10**). The OAc peaks were revealed is a singlet at 24.5 (**9**) and 26.7 ppm (**10**). The resonances for the methyl groups on the Cp* appeared at 9.43 (**9**), 9.38 ppm (**10**).

Upon initial ^{1}H NMR observations, specifically in the 2.0-3.0 ppm region, there were three distinct peaks in the spectra. To differentiate and identify those peaks, a variable temperature (VT) NMR experiment was done. Upon heating a sample of **10**, it was observed that

three peaks coalesced into one peak that integrated for six hydrogens, suggesting one acetate environment at ~2.0 ppm (*Figure 2*). When heated, the energy barrier allows ligand exchange to occur. This is manifested when the three peaks coalesced into one, which is a time average of the three signals.

Furthermore, a ^{1}H-^{13}C HMQC NMR analysis confirmed the consistency of the observed data from ^{1}H (VT) and ^{13}C NMR spectra of **10**. This analysis affirmed that the peak at 2.20 ppm was the acetate peak (*Figure 3*). However, based on the elemental analysis data from **7** and **8**, it is possible that there is also innersphere-outersphere ligand coordination exchange among the I, OH_2, and OAc in the solution, resulting in hydrate isomers. This will be further explored in the future.

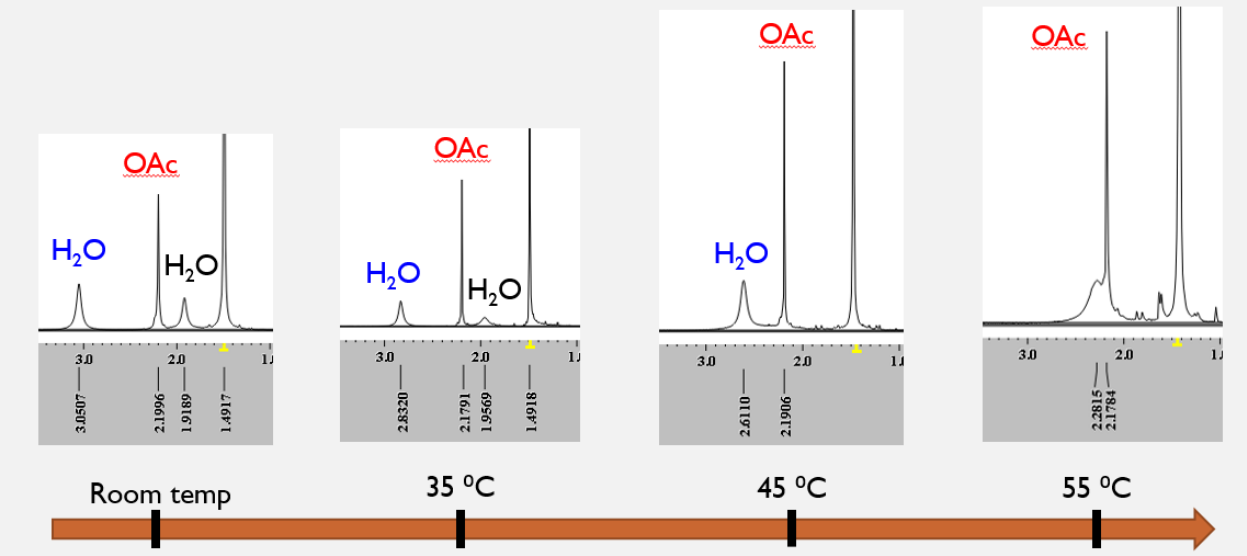


Figure 2. VT of [Co(Cp)(S,S-DPEN)(OH_2)]($OAc)_2$ · nH_2O*

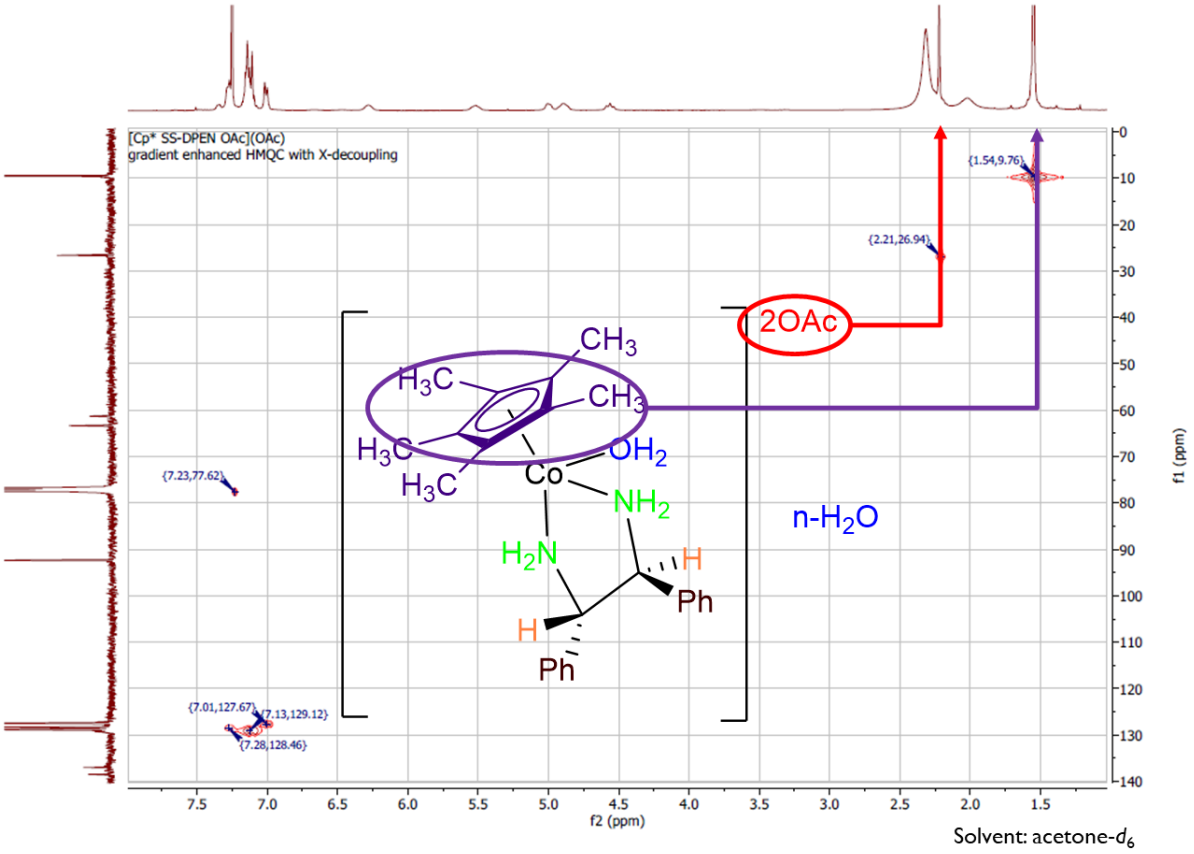
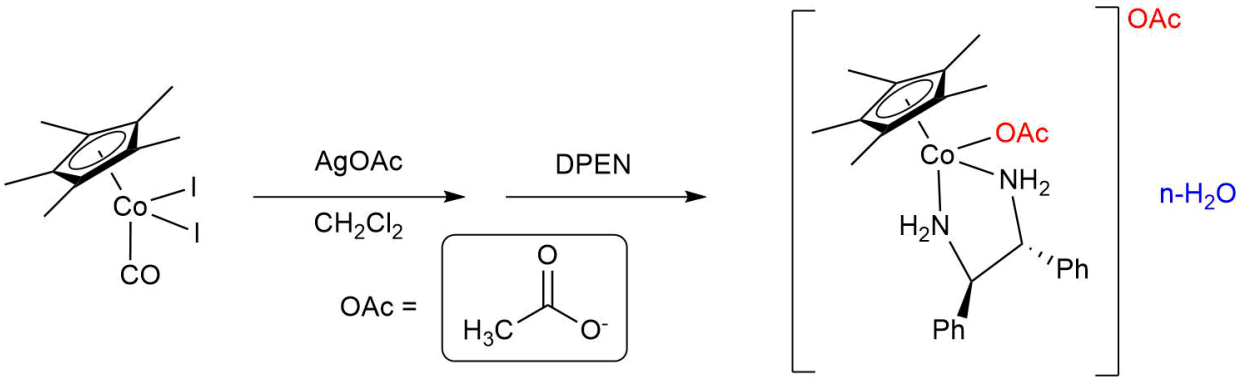


Figure 3. ^{1}H-^{13}C HMQC of $[Co(Cp^*)(S,S\text{-}DPEN)(OH_2)](OAc)_2 \cdot H_2O$

Synthesis of [Co(Cp*)(R,R -DPEN)(OAc)](OAc) · nH_2O **(11)**



Scheme 6. Synthesis of [Co(Cp)(R,R-DPEN)(OAc)](OAc) · nH_2O*

To determine if the water/dichloromethane solvent mixture was necessary for the synthesis of the acetate complexes, our group explored a different synthetic pathway. Reacting [Co(Cp^R)(CO)$(I)_2$] with AgOAc followed by DPEN addition, with only dichloromethane as the solvent, produced the complex [Co(Cp*)(R,R-DPEN)(OAc)](OAc) · nH_2O. Complex **11** was confirmed by ^{1}H, VT-^{1}H, ^{13}C NMR, and ^{1}H-^{13}C HMQC. The ^{1}H NMR spectra revealed a singlet at 1.55 ppm, integrating for fifteen protons, which corresponds with the Cp* analogue. Two methine protons from the DPEN resonances were revealed at 4.94 and 4.58 ppm as triplet of doublets. The triplet rises from the CH coupling to the amine protons and the doublet from coupling to one adjacent CH proton. The OAc resonance appeared as two sharp singlets at 2.23 and 1.92 ppm as well as abroad singlet at 2.79 ppm, *vide infra*. The ^{13}C NMR spectra revealed a singlet at 92.3 ppm, which corresponds with the Cp* aromatic ring. Two methine carbon resonances appeared at 63.2 and 60.9 ppm. The OAc peak resonates as a singlet at 26.7 ppm. The resonances for the methyl groups on the Cp* appeared at 9.42 ppm.

Upon initial ^{1}H NMR observations, there were three peaks downfield to the Cp* analogue that had ambiguous identities. To differentiate and identify those peaks, a variable temperature

(VT) NMR experiment was done. Upon heating a sample of **11**, it was observed that three peaks coalesced into two distinct peaks that integrated for six hydrogens, suggesting two OAc environments at 2.20 and 2.52 ppm that may interchange with the I for innersphere coordination in solution (*Figure 4*). Furthermore, a ^{1}H-^{13}C HMQC NMR analysis confirmed the consistency of the observed data from ^{1}H (VT) and ^{13}C NMR spectra of **11**. This analysis affirmed that the peak at 2.20 and 2.52 ppm were the acetate peaks (*Figure 5*)

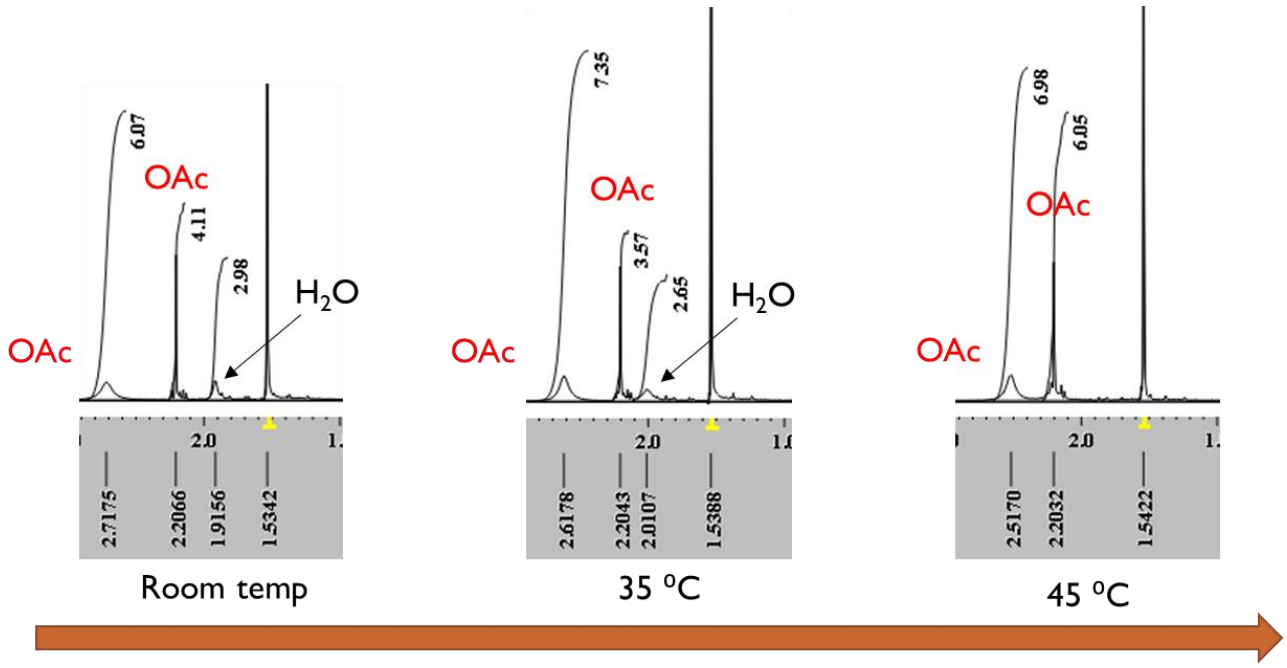


Figure 4. VT of [Co(Cp)(R,R-DPEN)(OAc)](OAc) · nH_2O*

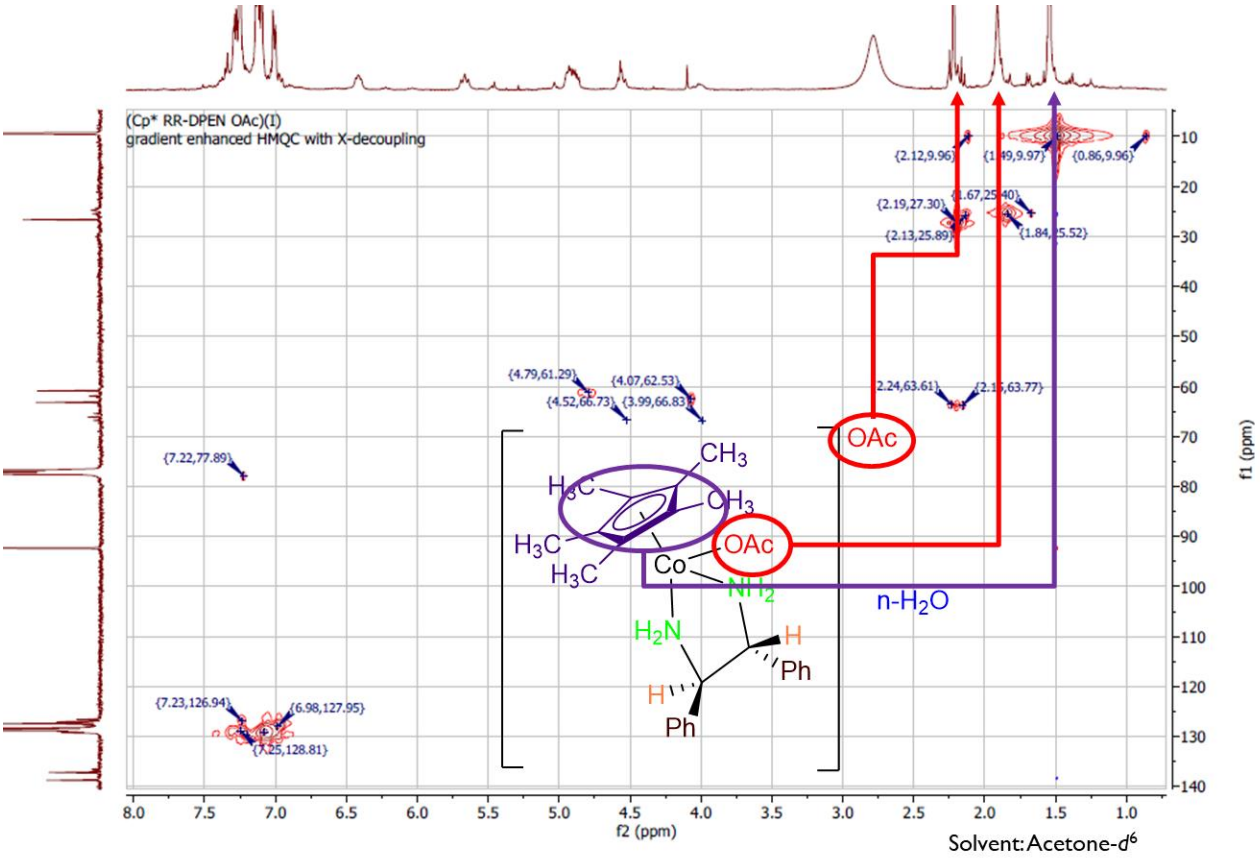
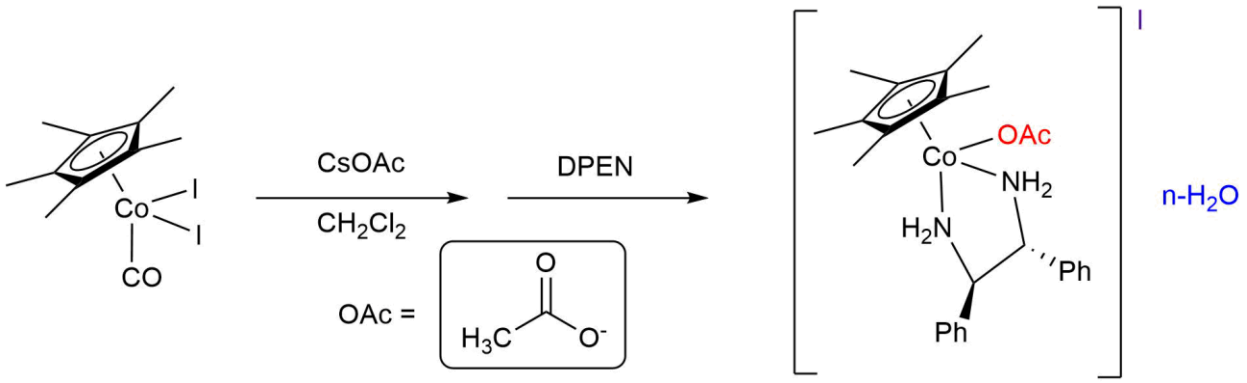


Figure 5. ^{1}H-^{13}C HMQC of [Co(Cp)(R,R-DPEN)(OAc)](OAc) · nH_2O*

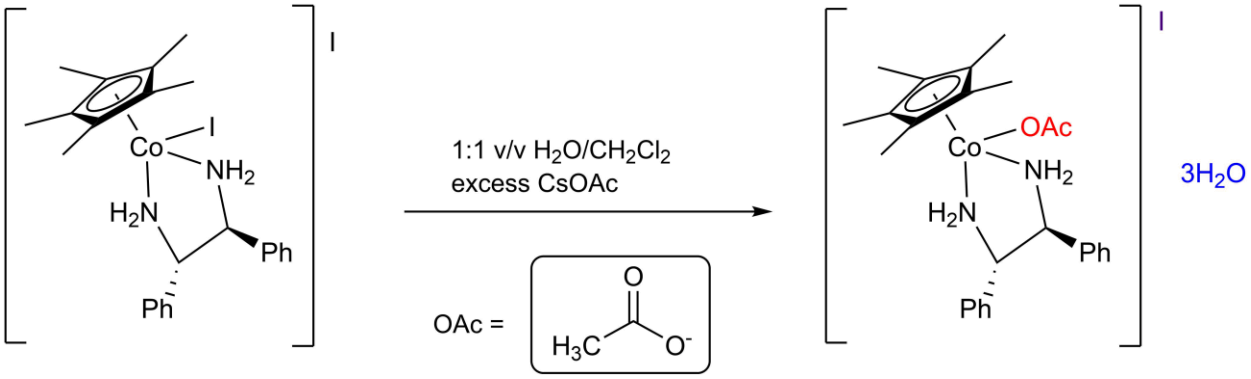
Synthesis of [Co(Cp*)(R,R-DPEN)(OAc)](I) · nH_2O (**12**)



Scheme 7. Synthesis of [Co(Cp)(R,R-DPEN)(OAc)](I) · nH_2O*

Our group then explored the addition of CsOAc to the complex $[Co(Cp^R)(CO)(I)_2]$ in dichloromethane. This reaction displaced the iodide from the innersphere and an OAc molecule coordinated to the metal. The iodide relocated to the outersphere. Complex **12** was confirmed by ^1H and ^{13}C NMR. The ^1H NMR spectra revealed a singlet at 1.53 ppm, integrating for fifteen protons, which corresponds to the methyl resonances on the Cp*. Two methine protons from the DPEN resonances were revealed at 4.89 and 4.53 ppm. Also, at 4.89, there appears to be overlap of the amine protons, which is why ^1H reveals two protons in that region instead of one. This behavior is typical for these complexes. The OAc resonance appeared as sharp singlet at 2.23 as well as abroad singlet at 1.96 ppm. ^{13}C NMR analysis for this complex will be explored in the future.

Synthesis of [Co(Cp*)(S,S -DPEN)(OAc)](I) · $3H_2O$ (**13**)



Scheme 8. Synthesis of [Co(Cp)(S,S-DPEN)(OAc)](I) · $3H_2O$*

An alternative synthetic pathway to obtain [Co(Cp*)(X,X-DPEN)(OAc)](I) · nH_2O is by reacting [Co(Cp^R)(X,X-DPEN)(I)](I) with CsOAc in a water/dichloromethane solvent mixture. Complex **13** was confirmed by ^1H and ^{13}C NMR. The ^1H NMR spectra revealed a singlet at 1.62 ppm, integrating for fifteen protons, which corresponds with the Cp* analogue. Two methine protons from the DPEN resonances were revealed at 4.98 and 4.40 ppm. Also, in the 4.40 region, there appears to be overlap of the amine protons, which as previously noted before, this shifting is typical behavior. The OAc resonance appeared as sharp singlet at 2.23 as well as abroad singlet at 1.96 ppm. The ^{13}C NMR spectra revealed a singlet at 93.0 ppm integrating for five protons, which corresponds with the Cp* aromatic analogue. The two methine carbon resonances appeared at 63.5 and 62.4 ppm. The OAc peak was revealed a singlet at 26.5 ppm. The resonances for the methyl groups on the Cp* appeared at 10.7 ppm.

An attempted crystallization was successful and x-ray crystallographic data was obtained. A summary of the bond lengths and angles are listed in *Table 2*. As shown in *Figure 6*, the crystal structure revealed a coordinated acetate with iodide in the outer sphere. The asymmetric unit cell contains two complex cations linked through H-bonding water molecules. There are three aqua ligands for each cation making a total of six aqua molecules per unit cell. The coordinated acetate H-bonding to the DPEN resulted in a boat conformation of a 6-membered ring. From this data, it appears that silver is necessary for the complete removal of the iodide.

Table 2. Crystallography Data for [Co(Cp)(S,S-DPEN)(OAc)](I) · 3H_2O*

(**13**)				
Distances (Å)				
Co-O1	1.998 (8)			
Co-N1	1.998 (9)			
Co-N2	1.992 (9)			
Angles (°)				
N1-Co-N2	83.3 (4)			
I1-Co-N2	92.9 (4)			
I1-Co-N1	86.4 (4)			
Hydrogen Bonds				
D H A	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
N1-H1A-O5A	0.91	2.25	3.075 (15)	150.0
N1-H1B-O4	0.91	2.11	3.006 (14)	170.4
N2-H2A-O3	0.91	2.05	2.907 (14)	156.6
N2-H2B-O2	0.91	2.11	2.853 (13)	138.4
O5A-H5AA-O1	0.87	2.03	2.852 (13)	156.6

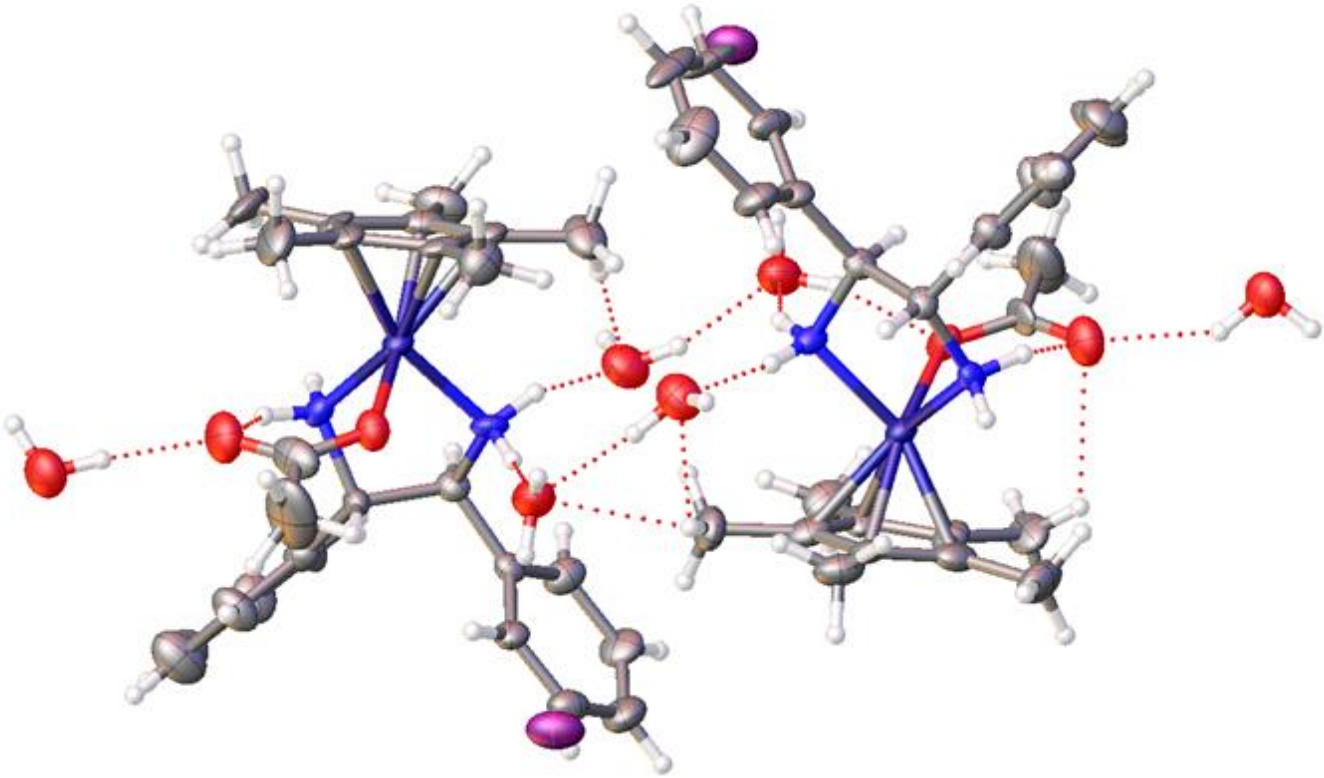
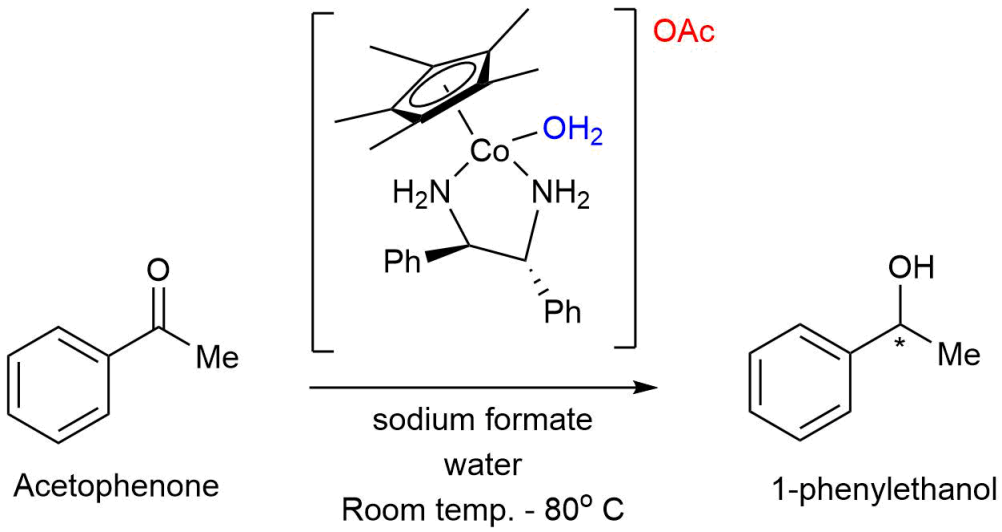


Figure 6. Crystal structure of [Co(Cp)(S,S-DPEN)(OAc)](I) · $3H_2O$ (**13**) revealing an asymmetric unit cell linked through H-bonding.*

4. Results and Discussion – Part 2 Reactivity



Scheme 9. Transfer Hydrogenation of Acetophenone

To explore the reactivity of the acetate complexes, transfer hydrogenation of acetophenone were attempted. A summary of attempted reactions are shown in *Table 3*.

Table 3. Transfer Hydrogenation of Acetophenone Attempts

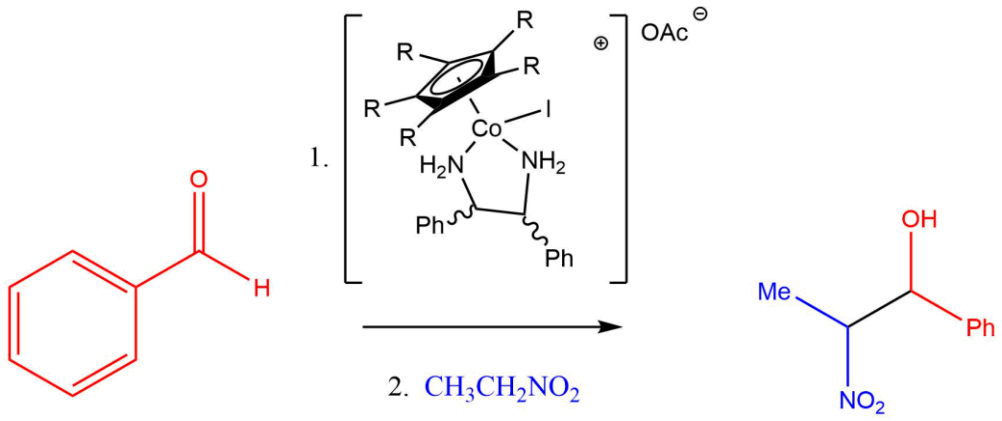
Reactant/Solvent	**Catalyst**	**Temperature**	**Product(s)**
$HCOONa/H_2O$	**7**	75 °C	No reaction
$HCOONa/H_2O$	**7**	80 °C	No Reaction
Azeotrope*	**9**	40 °C	No Reaction

*5:2 molar ratio of formic acid and triethylamine

In previous work by Uematsu *et al*., chiral Ru(II) complexes that catalyze the asymmetric reduction of imines with formic acid/triethylamine azeotrope under mild conditions were developed.[12] Since the acetate complexes are soluble in water and since aqueous catalysis of transition metals are known by previous experimentation, it was in our interest to explore reactivity of our acetate complexes. We began our study by using sodium formate as a hydrogen

source in aqueous solvent to assist in catalyzing the substrate, acetophenone. The expected product was 1-phenylethanol. The first attempt, with a reaction temperature of 75 $^{\circ}$C, resulted in no reaction per ^{1}H NMR. In another attempt, when heated to 80 $^{\circ}$C, there was also no reaction. A third attempt involved the use of an azeotropic mixture of formic acid and triethylamine as the reactant and solvent, and heating the solution to 40 $^{\circ}$C. There was also no desired product as indicated by ^{1}H NMR. A probable reason for the complex impotency can be explained by the VT NMR studies that were previously done on the complexes. When heating the complex above 45 $^{\circ}$C, it becomes unstable and decomposes. These reactions might require some heat to overcome an activation energy, which results in catalyst decomposition. Alternatively the complex is not reducing enough to remove a hydride from the formate and produce CO_2. For the first explanation it can be concluded that the acetate complexes were unstable and could not facilitate transfer hydrogenation reactions. For the second explanation, future work will involve exploring catalytic hydrogenation of CO_2, which would be the reverse reaction of transfer hydrogenation from formate, to see if the catalyst is competent for that reaction.

5. Conclusions and Future Work



Scheme 6. Nitroaldol Reaction of Benzaldehyde

Seven complexes of the types $[Co(Cp^R)(X,X\text{-}DPEN)(OH2)](OAc)_2 \cdot nH_2O$, [Co(Cp*)(R,RDPEN)(OAc)](OAc) · nH2O, [Co(Cp*)(R,R-DPEN)(OAc)](I) · nH_2O, and [Co(Cp*)(S,SDPEN)(OAc)](I) · $3H_2O$ have been synthesized successfully. These products can be obtained either by reacting $[Co(Cp^R)(X,X\text{-}DPEN)(I)](I)$ with AgOAc, in pot via reaction of $[Co(Cp^R)(CO)(I)_2]$ with AgOAc followed by DPEN addition, or $[Co(Cp^R)(CO)(I)_2]$ with CsOAc followed by DPEN addition. It appears that depending on solvent choice and/or reagent choice, produces variations of complexes. These include complexes with an iodide likely coordinated to the metal and two OAc in the outer-sphere; a complex with an aqua molecule coordinated to the metal and one OAc in the outer-sphere; and a complex with an OAc coordinated to the metal and an iodide in the outer-sphere.

^{1}H-VT, ^{13}C, HMQC NMR spectroscopy as well as Single Crystal X-Ray Crystallography confirm the presence of acetate and aqua molecules in the complex. Elemental analysis confirms the presence of iodide in the majority of the complexes, although synthetic details should be explored further to understand the nature of these acetate complexes. The cesium acetate

complexes still need to be characterized further. VT-NMR and attempted transfer hydrogenation reactions reveal OAc complex instability or the complex is not reducing enough to remove a hydride from the formate and produce CO_2. Future work will be determining the reactivity limits of the complexes via catalytic reduction of CO_2 or attempting the nitroaldol reaction of benzaldehyde in aqueous solution (*Scheme 6*).[13]

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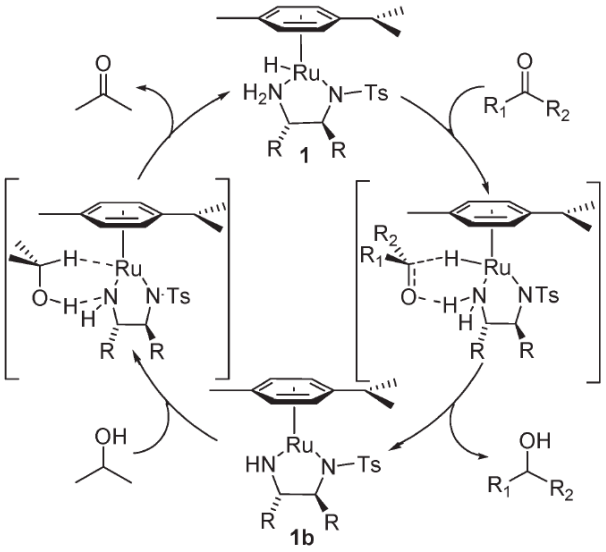
Chapter 4: Synthesis and reactivity of Co(III) complexes bearing a Ts-DPEN ligand

1. Introduction

Though catalysis was not observed with the acetate complexes to facilitate transfer hydrogenation reactions, their unique solubility gives room for more research projects. Nonetheless, it was in our interest to explore the possibility of utilizing the Ts-DPEN [*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine] ligand, which has been shown to catalyze transfer hydrogenation reactions of ketones.[1] Early experiments with this ligand involved the use



Scheme 1. Ru Catalyzed Transfer Hydrogenation of Ketones.[2]

of $[RuCl_2(benzene)]_2$ mixed with a base in 2-propanol. Later experiments revealed the proposed mechanism of the catalytic reduction of ketones and imines using [Ru(*p*-cymene)(Ts-DPEN)(H)] in 2-propanol that involved a concerted cycle. A variety of chiral alcohols were produced in high yields and *ee* (*Scheme 1*).[2,3] The proton transfer from the hydride and the NH_2 to the substrate gives a cyclic six-membered transition state to produce an alcohol. The 2-propanol then supplies a hydride to the metal and a proton to the ligand, leaving acetone as a byproduct. There is no metal-substrate coordination in this proposed mechanism. The chiral ligand provides a chiral pocket for either the re or si face of the prochiral molecules, whether it is ketones being reduced to alcohols or imines to amines.[4] In contrast to ketone reduction, which requires 2-propanol,

reduction of imines are performed in an azeotropic mixture (5:2 molar ratio) of formic acid-triethylamine and has been shown to be catalyzed by Ru complexes with Ts-DPEN derivatives.[3] Although this reaction is historically catalyzed by precious metals in combination with the Ts-DPEN ligand, it is hypothesized that an extension to octahedral Co(III) would be feasible. Therefore, our group set out to prepare and study the reactivity of the Ts-DPEN with Co(III). The syntheses and reactivities will be discussed in this chapter.

2. Experimental Section

2.1. Materials

All solvents and reagents were used as received. The ligand (R,R)-TsDPEN was purchased from Alfa Aesar and used as received. The metal reagents $[Co(Cp)(CO)(I)_2]$ and $[Co(Cp^*)(CO)(I)_2]$ were prepared as previously reported.[5,6] GC-MS spectra were obtained from Trace GC Ultra Gas Chromatograph. A Thermo Polaris Q Mass Spectrometer was used to determine molecular weights.

2.2. Measurements

^1H and ^{13}C NMR spectra were obtained on a JEOL ECX 400 MHz spectrometer (operating frequency for ^{13}C NMR was 100 MHz) and referenced against tetramethylsilane using residual proton signals (^1H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). Elemental analyses were performed by Atlantic Microlab, Inc in Norcross, GA.

2.3 Syntheses

5.3.1. Preparation of [Co(Cp)(R,R-Ts(H)DPEN)(I)](I) (**14**).*

In a nitrogen filled glovebox, a 50 mL round-bottom flask was charged with [Co(Cp*)(CO)$(I)_2$] (0.0507 g, 0.107 mmol), dichloromethane (25 mL), and (R,R)-Ts(H)DPEN (0.0469 g, 0.128 mmol) There was a slight color change from dark purple to a lighter purple. The mixture was stirred at room temperature for about 16 h. The solvent was removed *in vacuo* and the resulting product was washed with hexanes. The recovered green/gray product had a final product weight of 0.0741 g. (85% yield). ^{1}H NMR (87a-1H-LD), ^{13}C NMR (87a-13C-LD). ^{1}H NMR (acetone-d_6, δ): 7.05-7.49 (20H, m, Ts-DPEN aromatic and NH), 4.70 (2H, m, CH), 2.23 (15H, s, Cp*), 1.26 (3H, s, Ts-CH_3). ^{13}C {^{1}H} NMR (acetone-d_6, δ): 142.4 (1C, s, ipso *C* arene), 129.1, 128.3, 127.9, 127.8, 127.8, 127.7, 127.6, 127.4, 127.3, 127.1, 126.8 (11C, m, Aromatic *C* DPEN), 102 (5C, s, *Cp*), 71.9 (1C, s, DPEN CH), 69.1 (1C, s, DPEN CH), 20.3 (1C, s, Ts-CH_3), 10.6 (5C, s, Cp* CH_3).

5.3.2. Attempted Preparation of [Co(Cp)(R,R-TsDPEN)(I)] (**15**).*

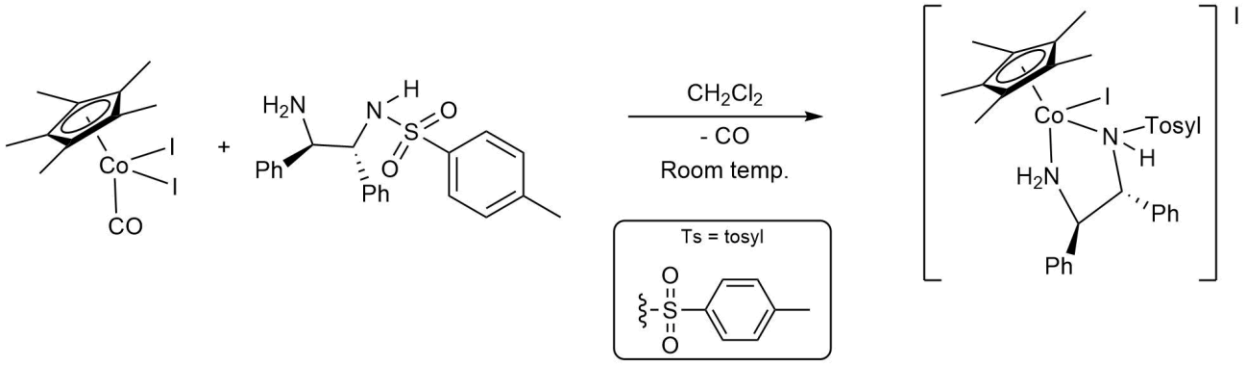
A 50 mL round-bottom flask was charged with **14** (0.0250 g, 0.0307 mmol), dichloromethane (5 mL), and KOH (0.0260 g, 0.463 mmol) Upon vigorous stirring, after 5 min, H_2O was added (5 mL). The aqueous layer changed to purple color. After 10 min, the organic layer began to turn yellow/green. The layers were separated into two separate evaporating dishes. The product from the organics that remained was a green/gray color. The final product weighed 0.0107 g. ^{1}H NMR (94a-1H-LD). The NMR spectra revealed that the complex was paramagnetic, and therefore there were no significant peaks to be observed.

5.3.3. Attempted Transfer Hydrogenation of Acetophenone

In a fume hood, a 3 mL conical flask was charged with formic acid/triethylamine (5:2 mol). The mixture was let to react for 5 min and then cool to room temperature. **14** (0.00820 g, 10 µmol) was then added. There was a color change from brown to dark blue. The flask was then charged with acetophenone (0.12 mL, 1 mmol) and the solution began to stir at room temperature. After 1 h, the solution color changed to light pink. The solution stirred for 48 h and was then transferred into a 10 mL round-bottom flask. The solution was dissolved in 2 mL ethyl acetate (EtOAc) and washed with 2 mL $NaHCO_3$ (10%). The organic layer was separated and placed in an evaporating dish. There was no recorded yield. A ^{1}H NMR and GC-MS sample was taken and revealed no indication of 1-phenylethanol.

3. Results and Discussion – Part 1 Synthesis and Characterization

Synthesis of [Co(Cp*)(R,R-Ts(H)DPEN)(I)](I) (**14**)

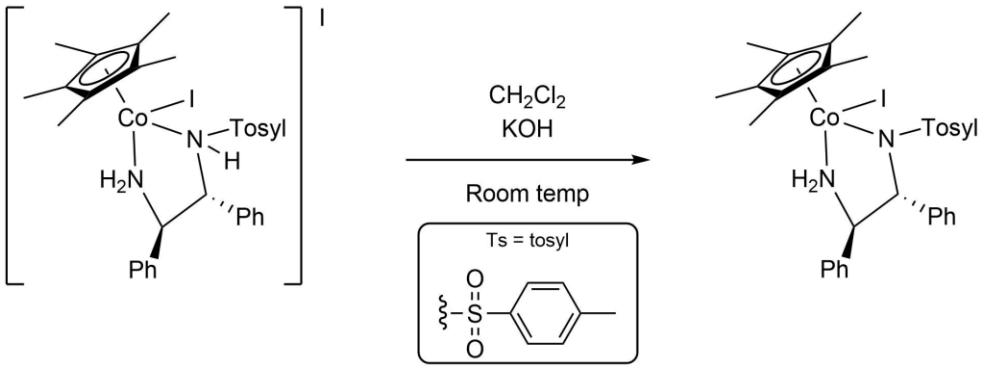


Scheme 2. Synthesis of [Co(Cp)(R,R-Ts(H)DPEN)(I)](I)*

It was initially hypothesized that the Co(III) complex bearing the Ts-DPEN ligand would be synthesized in an alcohol mixture with triethylamine under refluxing conditions.[4] This would deprotonate the amine, making the overall complex neutral. However, ^{1}H NMR data suggested

the complex was likely reduced to paramagnetic Co(II). We decided to synthesize the complex similar to our original iodide complexes. Therefore, [Co(Cp*)(CO)$(I)_2$] was reacted with excess Ts-DPEN in dichloromethane. This synthetic route allowed for the formation the stable cationic complex **14**. The results were confirmed by ^{1}H and ^{13}C NMR. The ^{1}H NMR spectra revealed a singlet at 2.23 ppm, integrating for fifteen protons, which corresponds with the methyl groups on the Cp* ligand. The Ts-CH_3 resonance appeared as a singlet at 1.26 ppm. The two methine protons from the DPEN ligand appeared at 4.70 ppm and integrated for two protons. The amine protons appear to be buried in the aromatics region. The ^{13}C NMR spectra revealed a singlet at 102 ppm which corresponds with the Cp* aromatic ring. The two methine carbon resonances were confirmed and appeared at 71.9 and 69.1 ppm. The Ts-CH_3 peak was revealed as a singlet at 20.3 ppm. The resonances for the methyl groups on the Cp* appeared at 10.6 ppm.

Synthesis of [Co(Cp*)(R,R-TsDPEN)(I)] (**15**)

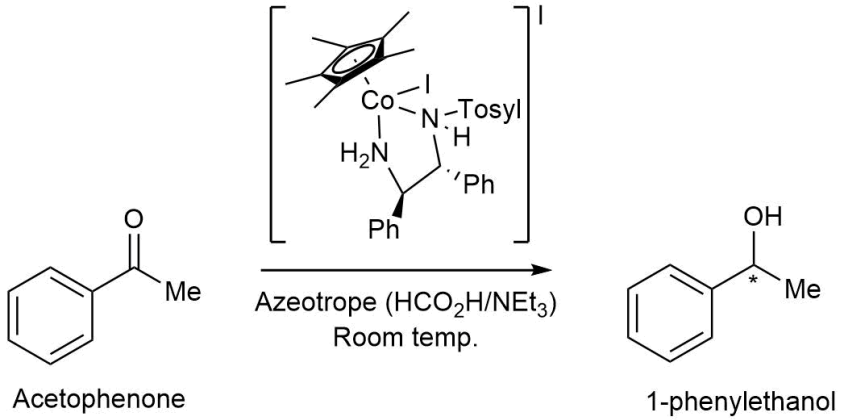


Scheme 3. Synthesis of [Co(Cp)(R,R-TsDPEN)](I)*

With the successful product isolation of cationic [Co(Cp*)(R,R-Ts(H)DPEN)(I)](I), it was in our interest to continue the attempts at deprotonating the complex to synthesize the desired neutral variant of the complex. The synthesis of complex **15** was attempted by reacting **14** under basic conditions. The product was analyzed by ^{1}H NMR. The spectra did not reveal any

significant peaks. The Cp* resonance did not appear at all. This suggests the complex was likely reduced to Co(II) and thus paramagnetic. Therefore, the addition of a strong base under the conditions experimented was shown to be an ineffective way to deprotonate the secondary amine on the Ts(H) DPEN ligand.

4. Results and Discussion – Part 2 Reactivity



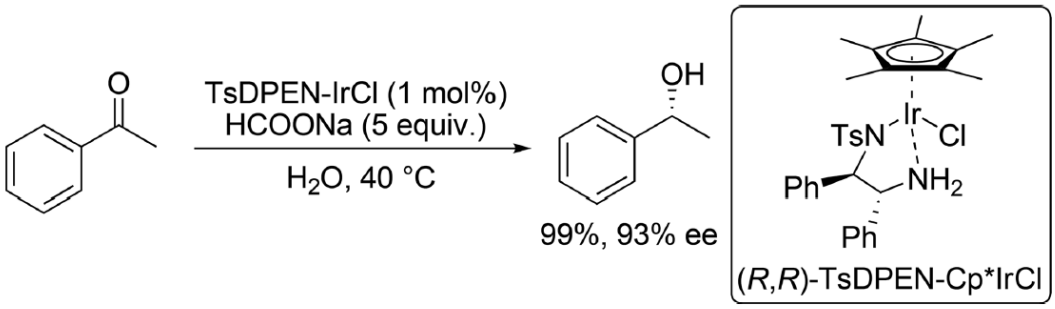
Scheme 4. Transfer Hydrogenation of Acetophenone

Catalytic asymmetric transfer hydrogenation of acetophenone was attempted using **14** as the catalyst. Per ^{1}H NMR, a quintuplet was revealed at 4.6 ppm which corresponds to the CH_3. However, the acetophenone peak was ambiguous. A sample of the product was analyzed on the GC-MS. A peak on the chromatogram at 5.40 min revealed a m/z that accounted for acetophenone. There was no evidence of 1-phenylethanol, the desired product.

5. Conclusions and Future Work

The synthesis of complexes of the type [Co(Cp*)(Ts-DPEN)(I)](I) was attempted. There is evidence in the successful synthesis and stability of the cationic variant, [Co(Cp*)(R,R-Ts(H)DPEN)(I)](I), as revealed by both ^{1}H and ^{13}C NMR. Attempts to deprotonate the complex,

however, were inconclusive. Furthermore, attempts to use the cationic complex **14** for the catalytic reduction of acetophenone revealed no evidence of the desired product, 1-phenylethanol. The next step will be to continue attempts to deprotonate the cationic variant under the most favorable conditions.



Scheme 5. Ir Catalyzed Transfer Hydrogenation of Acetophenone.[13]

The reactivity of these complexes to be used as a catalyst is also another step in the continuation of this project. In our attempts, an azeotropic mixture of formic acid and triethylamine was used as the solvent and hydrogen source for the catalytic cycle. As this is the most commonly used solvent for the hydrogen transfer of ketones and imines using the Ts-DPEN, literature studies reveal the reaction rates using this methodology are slow.[7] In fact, when the ratio of formic acid and triethylamine is lowered, the reaction rates increase.[8,9,10] Also, it was also reported that asymmetric hydrogen transfer using the Ts-DPEN ligand with water as the solvent increases the reaction rate and is pH dependent.[11] It is evident then, that higher pH favors both higher reaction rates and enantioselectivities.[12] Since the catalytic reduction of acetophenone in aqueous conditions using Ts-DPEN ligand was successful using Ir (*Scheme 5*),[7,13] it will therefore be beneficial to utilize reaction conditions to an aqueous environment for the future work of our complexes.

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Appendix A: Crystallography Data

Table 1 lists the crystallography data for compounds **1**, **2a**, **4**, and **13**.

Table 1. Crystallography Data for Co(III) complexes

	(**1**)	(**2a**)	(**4**)	(**13**)
Formula	$C_{19}H_{21}CoI_2N_2$	$C_{50.99}H_{34}BCoF_{23.96}IN_2$	$C_{25}H_{33}Cl_2CoI_2N_2$	$C_{26}H_{40}CoIN_2O_5$
Habitat, color	block, purple	block, purple	block, purple	block, purple
Lattice type	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a, Å	11.3756(13)	9.9712(15)	9.3568(10)	16.336(6)
b, Å	9.1572(9)	20.987(3)	14.7801(18)	10.278(4)
c, Å	20.313(2)	25.671(4)	21.124(2)	19.017(8)
V (Å^3)	2059.8(4)	5372.0(13)	2921.3(6)	3000(2)
Z	4	4	4	4
Fwt., g mol^{-1}	590.11	1326.58	745.16	646.43
D_c, g cm^{-3}	1.903	1.640	1.694	1.431
μ (mm^{-1})	3.834	1.015	2.899	1.635
T (K)	200(2)	200.15	200.15	200.15
Reflections collected	22503	58804	30002	55951
Unique reflections	6418 [R_{int} = 0.0481]	9486 [R_{int} = 0.0554]	5167 [R_{int} = 0.0681]	10596 [R_{int} = 0.2355]
Data, restraints, param.	6418/1/433	9486/0/726	5167/0/294	10596/1/661
R_1, wR_2 (I > 2s(I))	0.0345, 0.0749	0.0395, 0.0939	0.0273, 0.0518	0.0589, 0.1324
R_1, wR_2 (all data)	0.0427, 0.0787	0.0489, 0.0995	0.0324, 0.0533	0.0809, 0.1455
Goodness-of-fit (F^2)	1.066	1.018	0.995	1.019
largest diff. peak, hole, e Å^{-3}	1.03/-0.43	0.61/-0.41	0.44/-0.41	1.08/-1.53
Flack parameter	-0.01(3)	-0.013(7)	-0.012(12)	-0.01(3)

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